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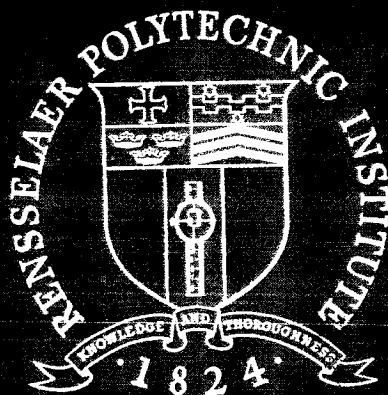
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Rensselaer Polytechnic Institute

Troy, New York

INFRARED AND PROTON NMR  
STUDIES OF  
METALLIC ACETATE COMPLEXES

by

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Submitted

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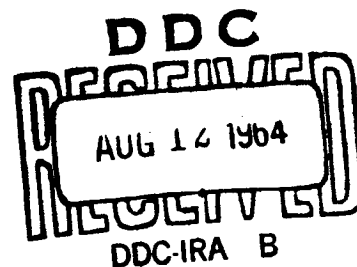
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## ABSTRACT

The infrared spectra of 20 metallic acetate complexes have been measured from 2.5 to 40 microns at room temperature and at liquid nitrogen temperature. Fifteen of the complexes studied occur as hydrates, while five exist as the anhydrous compounds.

This study is concerned primarily with the infrared absorption of the coordinated water molecules that are present in the hydrated complexes.

Integrated proton nuclear magnetic resonance spectra have been obtained in order to determine the number of coordinated water molecules present per molecule of acetate. Delta values have been measured for the  $\text{CH}_3$  and  $\text{H}_2\text{O}$  peak positions at room temperature using capillary tetramethylsilane as the reference standard.

A procedure is given for the preparation of deuterated hydrates in all cases where a normal hydrate exists. The normal hydrates were dehydrated in an effort to distinguish the absorptions of the coordinated water molecules. The spectra of the anhydrous, dehydrated, hydrated, and deuterated hydrates are compared at room temperature and at liquid nitrogen temperature from 2.5 to 40 microns in an effort to assign all

vibrations of the coordinated water molecules. All absorption bands in the sodium chloride and cesium bromide regions are assigned and intensity data are given.

In a few cases X-ray diffraction data were available concerning the structures of the hydrated acetate complexes. In these cases the infrared analysis was compared with the X-ray structures in an effort to learn more about the nature of the bonding in these hydrates.

Free water protons were detected in three of the tetrahydrate acetates while the remaining water protons were found to be important in the formation of hydrogen bonds. Intra- and inter- molecular hydrogen bonds were found to be present in some cases. Low temperature infrared analysis showed the broad hydrogen bonded water stretching absorption to actually split into several distinct peaks characteristic of the type of hydrogen bonded water present.

Other than the  $\text{H}_2\text{O}$  stretching and bending absorptions, bands were found in some of the hydrates in the  $700 - 900 \text{ cm.}^{-1}$  region which are assigned as rocking, twisting, or wagging modes characteristic of coordinated water molecules. Coordinated water absorptions in the cesium bromide region are assigned to a librational motion of the coordinated water. Discussions have been given in terms of coordination and hydrogen bonding.



No absorption was found in any of the acetate complexes that could be assigned to a metal-oxygen linkage. The metal-water bonds were found to vary from being probably essentially ionic in some hydrates to others which were found to possess some covalent character.

The infrared spectra of the acetates were obtained as Nujol and Fluorolube mulls, as powder films deposited from spectroscopic grade methanol, and by using the KBr pellet technique. Liquid nitrogen temperature spectra were also obtained using these techniques. No replacement or interaction with the matrix was found using the KBr pellet technique. Spectra obtained using all sampling techniques agreed well.

Vibrations of the acetate group are found to be fairly standard from complex to complex. The  $1300 - 1500 \text{ cm.}^{-1}$  acetate absorption, which occurs as a broad doublet at room temperature, was found to split into the four characteristic acetate frequencies in this region at liquid nitrogen temperature. A series of weak acetate peaks occur in the  $250 - 350 \text{ cm.}^{-1}$  segment of the cesium bromide region. These absorptions, which are present in the anhydrous, dehydrated, hydrated, and deuterated hydrates, do not show any sharpening or intensification at liquid nitrogen temperature and, if at all, appear more undefined than at room temperature. These absorptions are tentatively assigned to a librational motion of the whole molecule within the crystal lattice.

## PART I

## INTRODUCTION

A. Historical Review

Over the past decade infrared spectroscopy has found an increasingly greater number of applications in the structural examination of inorganic compounds. It should yield a great deal of information concerning the bonding and structure of metallic acetate complexes. Originally inorganic compounds did not readily lend themselves to infrared analysis as did organic compounds.<sup>31</sup> This was due, however, not to the nature of inorganic materials, but to instrumental limitations and to the lack of sufficient sampling methods for the crystalline state which existed in earlier years. With the advent of commercially available high resolution spectrophotometers and more refined methods of sample preparation infrared analysis became more applicable to the examination of inorganic and coordination compounds. Lecomte and his co-workers<sup>45,46,47</sup> contributed to the revival of interest in this field.

In 1952, Miller and Wilkins<sup>58</sup> presented the infrared spectra of 159 pure inorganic compounds. Most of these are salts containing polyatomic ions. A table of characteristic

frequencies for 33 polyatomic ions was given. From this study it became apparent that infrared spectroscopy would be a very valuable tool in the analysis of polyatomic inorganic ions.

An infrared spectroscopic method<sup>33,34</sup> has been reported for the qualitative and semi-quantitative analysis of the mineral constituents of rocks. The method consisted of grinding the rocks to a finely pulverized form and examining the powder as a film on sodium chloride windows. The constituents are determined by comparing the spectra of the rocks with those of the pure minerals.

In 1960, another paper by Miller and co-workers<sup>59</sup> appeared reporting the infrared spectra in the cesium bromide region of over 200 inorganic substances with a list of characteristic frequencies for twenty ions being given. Ferraro<sup>15</sup> points out further developments in the use of infrared spectroscopy in inorganic chemistry. In recent years the study of complex and coordination compounds by infrared methods has been viewed as a very powerful tool by many workers as evidenced by the appearance of many research papers in this field.<sup>44</sup>

Many complex molecules contain characteristic groups such as  $\text{CH}_3$ , whose group frequencies and approximate vibrational modes are reasonably well known in advance of calculation.

King and Crawford<sup>42</sup> presented a method whereby these group vibrations may be eliminated from the vibrational problem once and for all, in advance, and whereby the reduced problem of framework vibrations may be simply written down without considering the complete molecular problem. Constructions are given by which effective masses of the group atoms and adjusted group force constants may be determined such that a reduced secular equation for the framework vibrations alone may be derived. Summary charts of group frequencies have been published.<sup>4, 39</sup>

The vibrational problem has been treated<sup>10</sup> for molecules consisting of a framework to which are attached any number of symmetrical tops, such as methyl groups. The vibrational problem can be separated from the internal torsional and over-all rotation if the potential function is restricted so that the vibrational frequencies are independent of the torsion angles. The separation is effected by carrying out the normal coordinate treatment in the usual manner,<sup>87</sup> using the value zero for all force constants involving torsion angles. The frequencies will not depend on the particular equilibrium orientation assumed for the tops. Furthermore, the secular equation for the vibrational problem can frequently be factored to a greater extent than is indicated by the symmetry of the

rigid molecule.

The symmetry of a complex inorganic molecule is a very important factor in assigning allowed vibrations. This is particularly true of the nitrate ion which has been studied extensively by infrared techniques. A study of the nitrate ion<sup>13</sup> has been made in tri-n-butyl phosphate solvates;  $M(NO_3)_3 \cdot 3TBP$ ,  $M(NO_3)_4 \cdot 2TBP$  and  $MO_2(NO_3)_2 \cdot 2TBP$ , and the spectra of these solvates have been compared with those of the corresponding hydrates. It was observed that a considerable decrease in symmetry of the nitrate group occurs in going from the hydrate form to the TBP solvates. An examination of the infrared spectra of metallic nitrates<sup>14</sup> has shown that in progressing from a monovalent metallic nitrate to a tetravalent metallic nitrate, an increased lowering of the nitrate symmetry and a transition from a point group  $D_{3h}$  symmetry to a point group  $C_{2v}$  symmetry occurs. The degree of dissymmetry arising in these nitrates appears to be related in part to the ionic potential of the cation. The infrared spectra of a number of other nitrate-complexes of metals have been studied<sup>24</sup> between 4000 and 700  $cm^{-1}$ . Assignments have been made for vibrations characteristic of the coordinated nitrate group. Strong absorption bands, which do not occur in ionic nitrates, appear in the regions 1530-1480, and 1290-1250  $cm^{-1}$ . The absorption arising from the vibration  $\nu_1$ , theoretically

inactive for  $\text{NO}_3^-$  ion, occurs as a strong peak in the nitrate-complexes within the range  $1034 - 970 \text{ cm}^{-1}$  due to  $-\text{O}-\text{NO}_2$  stretching. The infrared spectra of uranyl nitrate di-, tri-, and hexa-hydrate<sup>26</sup> have been studied with nitrogen of normal isotopic composition and with nitrogen enriched in  $^{15}\text{N}$  and most absorption bands assigned. Uranyl nitrate hexahydrate is in most respects a typical ionic nitrate. The spectra of uranyl nitrate di- and tri-hydrate are similar to the spectrum of rubidium uranyl nitrate, and all three are closely related to the fluorescence spectrum of cesium uranyl nitrate, studied by Dieke and Duncan.<sup>11</sup> These spectra are all characteristic of compounds having coordinated nitrate- groups. Structures have been suggested for the di- and the tri- hydrate which account for the observed splitting of many of the bands. Infrared spectra for the anhydrous nitrates of manganese, copper, zinc, and mercury indicate the presence of covalent metal-nitrate bonds. The anhydrous nitrates of cobalt, silver, cadmium, and lead have spectra characteristic of the nitrate ion. Frequencies for the hydrated nitrates of iron, cobalt, nickel, copper, zinc, and cadmium have been compared with the anhydrous species. Hydrated thorium nitrate exhibits bands characteristic of a coordinated nitrate group.

Infrared spectra of transition metal nitric oxide

complexes involving the  $\text{NO}^-$  ion<sup>28</sup> and complexes involving donation from the  $\text{NO}^+$  ion<sup>50</sup> have been studied in an attempt to correlate the position of the N-O stretching frequencies with the nature of the binding of the nitric oxide group in the complexes.

Analysis of the infrared spectrum of gypsum<sup>30</sup> has made it possible to assign sixteen out of the eighteen internal fundamental modes of the two sulfate ions, and ten of the twelve internal fundamental modes of the four water molecules in the unit cell.

The infrared spectra of simple and complex carbonates<sup>25</sup> have been observed and compared with the spectra of simple acid, basic, and organic carbonates and characteristic frequencies have been assigned. Strong absorption bands, which are absent in the spectra of ionic carbonates, occur at 1577-1493, 1338-1272, and 1080-1020  $\text{cm}^{-1}$  in those of the carbonate complexes.

The infrared spectra of a number of compounds containing metal-oxygen double bonds<sup>3</sup> have shown that the presence of a metal-oxygen double bond can be correlated with a stretching frequency in the range 900-1100  $\text{cm}^{-1}$ . The potential diagnostic value of this band in inorganic chemistry has been shown with particular reference to metal oxygen systems wherein more than one type of bonding occurs.

Spectra of bis-(glycino)- copper (II) monohydrate and bis-(glycino)-nickel (II) dihydrate have added to the knowledge of the nature of chelation bonding.<sup>72</sup> A number of vibrations were assigned in these complexes and it was concluded that the resonance structure of the carboxylate ion is essentially maintained and the bond between the central metal ion of the complex and the carboxylate group is essentially ionic.

The results of studying the N-H stretching vibration in coordination compounds have shown<sup>74</sup> that coordination with metals by molecules containing H-N bonds results in a marked increase in absorption in the 3 micron region and in a decrease in the frequency of the H-N stretching vibration. The effects of hydration, hydrogen bonding, configuration of the complex, and the solvent on the character and position of the absorption peaks in this region have shown that the shift in the H-N stretching frequency on coordination increases with increasing charge on the complex and with increasing covalent character of the N-M bond. The spectra of salicylaldehyde complexes show that the nickel (II) and copper (II) complexes have a trans square planar configuration and that the N-Ni bond in this complex is revealed to be stronger than the N-Cu bond.

Infrared studies of some metal-urea complexes<sup>68</sup> show that urea forms nitrogen to metal bonds with Pt (II) and Pd (II),



and oxygen to metal bonds with Cr(III), Fe(III), Zn(II), and Cu(II). Infrared absorption spectra of metal-thiourea complexes<sup>90</sup> show that thiourea forms sulfur to metal bonds and that band assignments can be made using calculations involving normal vibrations.

The effect of coordination on the infrared spectra of ammine, rhodanato, and azido complexes,<sup>17</sup> considering the effect of the outer-ions has shown that the shift of the rocking vibration of coordinated ammonia in ammine complexes gives a measure of these effects. The C-N and N-N stretching frequencies of the rhodanato and azido groups have been compared in Cr(III) and Co(III) complexes and the results correlated to their stabilities.

Ueno and Martell<sup>75</sup> reported the infrared absorption frequencies for bisacetylacetone-ethylenediimine, bisacetylacetone-1, 2-propylenediimine, bisbenzoylacetone-ethylenediimine, bisbenzoylacetone-1, 2-propylenediimine, bisbenzoylacetone-1, 3-propylenediimine, bistrifluoro-acetylacetone-ethylenediimine, and many of the corresponding Cu(II), Ni(II), Co(II) and Pd(II) chelate compounds. Frequencies are assigned in most cases to bond or group vibrations, and replacement of the enolic hydrogen of the ligand by metal ions results in a shift of frequencies.

Three bands in the  $580\text{--}430\text{ cm}^{-1}$  region have been tentatively assigned to vibrations of covalent metal-ligand bonds.

Absorption spectra of several metallic acetyl-acetonates have been interpreted<sup>47</sup> in terms of the vibrations of the carbon chain and the  $\text{CH}_2$  or  $\text{CH}_3$  groups while taking into account the keto-enol isomerism. Changes in the spectra are caused by the presence of the metal and a cyclic formula is most probable. Infrared absorption of metal chelates of 1,3-diketones<sup>32</sup> show that several frequencies can be assigned and that the spectra can be related to the structure and stability of the complexes.

<sup>83</sup>  
Vedder and Hornig have observed that fine structure appears in the infrared spectra of  $\text{NH}_4\text{I}$  in the NaCl type phase upon sufficient cooling and that this fine structure can be correlated with a rotational motion of the  $\text{NH}_4^+$  ion. These same authors<sup>82</sup> have also given an explanation of the infrared spectra of crystals.

<sup>21</sup>  
A recent study of the infrared absorption spectra of water of crystallization in copper sulfate penta- and monohydrate crystals, from the point of view of effect of coordination and hydrogen bonding, shows structural differences and presents information concerning the binding state of the water molecules. The  $\text{H}_2\text{O}$  stretching absorptions compare with those of various

inorganic hydrated sulfates.<sup>20</sup> The spectra have been discussed with emphasis on the structures as determined previously by X-ray analysis. It is interesting to note that other than the H<sub>2</sub>O stretching and bending vibrations, there are absorptions in the 813-875 cm.<sup>-1</sup> region, that have been assigned to the H<sub>2</sub>O rocking modes characteristic of coordinated water.

Infrared absorption spectra of the water of crystallization in cobaltous chloride hexa- and dihydrate crystals<sup>22</sup> and in ferrous chloride tetrahydrate crystals<sup>23</sup> show water absorptions due to the H<sub>2</sub>O stretching and bending modes and also vibrations at 790-755 cm.<sup>-1</sup> and at 642 cm.<sup>-1</sup> assigned to the H<sub>2</sub>O wagging and rocking modes respectively. The infrared spectra of these hydrates have been explained in terms of their molecular structures as previously determined by X-ray diffraction methods.

Jones<sup>36</sup> studied the infrared spectra of a thin path of solid LiOH and LiOH .H<sub>2</sub>O (undeuterated, partially deuterated, and completely deuterated). The spectra indicate that both hydrogens from each water molecule are used to form strong hydrogen bonds in the hydrate. These results serve to substantiate the crystal structures which were previously determined by X-ray methods.

An infrared investigation of bound water in hydrates<sup>51</sup> compares the shifts in the position of the water absorptions in a series of crystalline salt hydrates. An earlier paper<sup>52</sup> studying

the infrared absorption of the water molecule in crystals was concerned with the  $H_2O$  stretching vibration in various salt hydrates but did not study the remainder of the infrared region. Another early study<sup>53</sup> of eight complex salt hydrates concerned with the  $H_2O$  stretching vibration showed from two to four distinguishable stretching modes in the 3 micron region. An explanation was attempted by comparison of the infrared spectra with the X-ray crystal structures.

The proton-proton separation in hydrated water in 10 compounds have been measured by the Pake method<sup>54</sup> using proton magnetic resonance. The mean value is  $1.595 \pm 0.003$  A with a range in values from 1.56 to 1.61 A. However, consideration of experimental error in individual values of the p-p separation indicates that this range does not prove that this separation varies between compounds. Thus it appears that intermolecular forces on the protons in the water molecule are not appreciable compared to intramolecular forces. The orientations of the water molecules have been determined and in every instance the orientation appears to be determined by formation of hydrogen bonds between the water oxygen and the nearest pair of electronegative atoms. Proton nuclear magnetic resonance techniques have become very valuable in the structural analysis of complexes.<sup>70</sup>

An attempt has been made to calculate the vibrational frequencies of water in aquo complexes,<sup>71</sup> with particular regard

to the shifts of the frequencies of the fundamental vibrations of the free water molecule. On the basis of the electrostatic model of a coordination molecule of the type  $M-H_2O$ , two different types of calculations have been carried out: (1) A potential function of the van Vleck-Cross type (J.Chem.Phys.1, 357(1933)) with additional terms corresponding to the electrostatic interactions between the metal ion and the coordinated water molecule has been developed in series of powers of the internal coordinates in order to obtain equilibrium positions and values of the force constants; these numerical values have been used to solve the vibrational problem by the usual methods of the F, G matrices; (2) a perturbation method with the eigenfunctions of the normal vibration of the free water molecule as unperturbed wave functions and the operator of the electrostatic interaction metal-water as the perturbation operator has been also used. Both types of calculations have led to the prevision that the two stretching frequencies of water are lowered in the aquo complexes by an amount of the order  $3-400\text{ cm}^{-1}$ , while the bending frequency is raised by a few tens of wavenumbers, and both calculated expectations agree very well with the experimental data.

Recently van der Elsken and Robinson<sup>81</sup> explained the spectra of hydrates in the  $300-600\text{ cm}^{-1}$  region as arising from the librational modes of the bound water molecules as shown unambiguously by the frequency changes on substitution of deuterium

oxide. The number of bands observed in this region indicate the number of water molecules with different crystalline environments.

The infrared spectra of thin films of  $H_2O$  and  $D_2O$  were measured<sup>27</sup> at various temperatures between 20 and -180 degrees centigrade. A strong absorption band due to the librational mode of the water molecule has its maximum around  $710\text{ cm}^{-1}$  in the liquid. In ice it is shifted to  $800\text{ cm}^{-1}$  at -15 degrees centigrade and to  $850\text{ cm}^{-1}$  at -170 degrees centigrade. The corresponding  $D_2O$  bands show the normal isotope shift.

Fujita, Nakamoto and Kobayashi have studied the infrared spectra of metallic complexes,<sup>17,18,19</sup> and point out that "it is well known that water vapor exhibits three fundamental bands; e.g., asymmetric and symmetric stretching and bending vibrations at 3756, 3652 and  $1595\text{ cm}^{-1}$  respectively. The absorption of water in aquo complexes will not differ greatly from the spectrum of the vapor state if the metal-oxygen bond is purely ionic. However, if the bond is covalent, we may expect new modes of vibrations such as wagging, twisting and rocking modes characteristic of coordinated water molecules. Therefore, an investigation of these bands in typical aquo complexes is of considerable interest because it provides much information on the nature of the metal-oxygen bond". These authors find considerable evidence for both covalent and ionic bonding in the hydrates studied. Activation of rocking, twisting or wagging modes of water, which occur in the

600-900 cm.<sup>-1</sup> region, give excellent evidence for a metal-oxygen bond possessing covalent character.

The infrared spectra of water and ice have been studied<sup>5,8,64,65</sup> in an attempt to specify the structure and nature of the bonding in these materials in the liquid and solid state.

Nakamoto and coworkers<sup>60</sup> have studied stretching frequencies as a function of distance in hydrogen bonds of crystalline materials. "Straight" hydrogen bonds exhibit approximately linear relations between X-H...Y distances and the X-H stretching frequencies, while "bent" hydrogen bonds show large deviation from the regular sequence with higher frequencies. The effects of formal charge or coordination number have been observed with respect to the crystal structure and the nature of hydrogen bonding in several compounds. Hydrogen bonding is a very important factor in determining structures and stabilities of complexes.<sup>69</sup>

1. Acetate Investigations. The vibrational spectrum of sodium acetate has been studied by Duval, Lecomte and Douville;<sup>12</sup> Childers and Struthers;<sup>9</sup> Jones and McLaren;<sup>37</sup> Wilmshurst;<sup>86</sup> and by Ito and Bernstein.<sup>35</sup> Jones and McLaren assigned acetate vibrations for sodium acetate and sodium acetate-d<sub>3</sub> by analogy with the partial normal coordinate analysis and assignments for nitromethane as given by Wells and Wilson<sup>84</sup> and for trideuteronitromethane as given by T. P. Wilson.<sup>88</sup> Nakamoto compares the spectra<sup>63</sup>

of  $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$  at room temperature in the rock salt region. Wiberley et al studied the spectra from 2 to 15 microns of fifteen inorganic acetates.

Paramagnetism and delta-bonding in anhydrous and hydrated copper (II) acetates suggests that a delta-bond is formed between adjacent copper atoms by lateral overlap of  $3d_{x^2-y^2}$  orbitals, the z axis being taken as along the line joining the copper atoms. Copper acetate, according to this hypothesis, is the first case in which a delta-bond is the sole direct link between two atoms.

The infrared spectra and structure of the crystalline sodium acetate complexes of U(VI), Np(VI), and Am(VI) have been studied with emphasis on the comparison of metal-oxygen bond distance and bond force constant in this series of complexes.

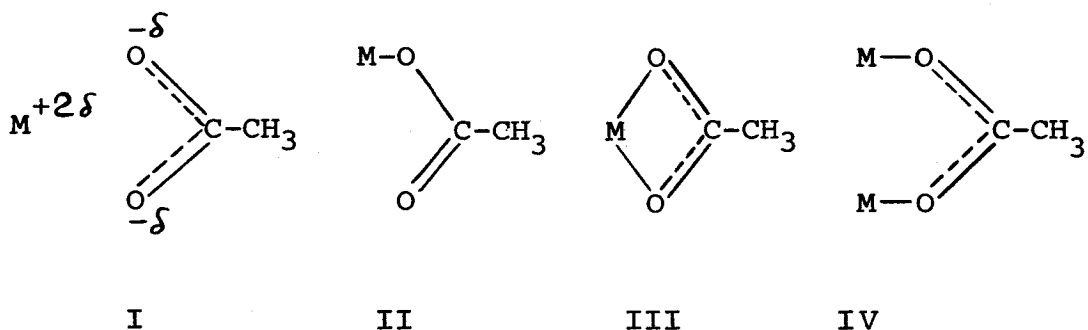
It has been shown that steroid acetates exhibit strong absorption between  $1200\text{--}1260\text{ cm}^{-1}$  and that there is a relationship existing between the number of bands appearing in this region and the cis or trans character of the structure.

Procedures have been given for the isotopic exchange of deuterium for hydrogen in the methyl groups of various acetates and the exchange reactions have been studied. It is interesting to note that two methods of approach are available for the synthesis of organic compounds containing deuterium. The first, the direct transfer by means of the exchange reaction, has been used,



for example, in the preparation of benzene-d<sub>6</sub>. It has the obvious disadvantage of requiring the depletion, in deuterium, of relatively large quantities of heavy water, and of making the removal of the last traces of ordinary hydrogen very difficult. The second method is the direct hydrolysis, hydrogenation or hydration of appropriate carbon compounds.

The acetate anion coordinates with a metal in one of the following ways:<sup>63</sup>



It has been found from X-ray analysis<sup>2</sup> that Li(CH<sub>3</sub>COO) · 2H<sub>2</sub>O has structure II, the two C-O bond lengths being different (1.33 and 1.22 Å). Structure II also occurs frequently among the salts of higher valency. Structure III is reported for Zn(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O<sup>79</sup> and Na(UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub>)<sup>91</sup>. Although this bidentate structure is less common than II, many anhydrous salts, such as Cr(CH<sub>3</sub>COO)<sub>3</sub> and Mn(CH<sub>3</sub>COO)<sub>3</sub>, may have structure III. With this structure maximum coordination number of the metal is satisfied. The unusual bridged structure IV was found in Cr<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub> · 2H<sub>2</sub>O<sup>76</sup>, Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub> · 2H<sub>2</sub>O<sup>77,80</sup>, Be<sub>4</sub>O(CH<sub>3</sub>COO)<sub>6</sub><sup>7</sup>.

and  $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$ <sup>43</sup>. Since the symmetry of the free ion ( $\text{C}_{2v}$ ) is low, no marked differences in the spectra would be expected for the various structures. The effect on the frequency of changing the metal, however, should be different for each structural type. For example, in a series of salts having structure II, the antisymmetric COO stretching frequency will increase, and the symmetric COO stretching frequency will decrease, as the M-O bond becomes stronger<sup>61</sup>. Such a trend is not seen, however, for a series of compounds having structure IV. Nakamoto and coworkers<sup>62</sup> have found that, in the symmetrical bridged structure IV, both the COO stretching bands are shifted in the same direction upon changing the metal.

#### B. Purpose Of This Research

The infrared spectra of complex and coordination compounds is very useful in determining the stability, structure, and the nature of bonding in these compounds. Few complete infrared investigations have appeared which have been solely interested in the absorptions due to coordinated water throughout the entire 2 to 40 micron region. Other than the spectra of anhydrous sodium acetate in solution and in crystal form, and the very few acetate spectra already noted,

the spectra of inorganic acetate complexes are not generally available.

The purpose of this investigation is to study an extensive series of metallic acetate complexes using infrared techniques throughout the region from 2 to 40 microns placing particular emphasis on the absorptions due to the coordinated water molecules in an attempt to characterize primarily water vibrations and secondarily acetate frequencies. The majority of the complexes studied here occur normally in the hydrated form and it is desired to study the spectra of these substances in the anhydrous, hydrated, and deuterated states as a further aid to the above mentioned objectives. Since very little information is available concerning the effect of temperature on acetate vibrations and no data have been reported dealing with the spectra of the complexes studied herein at lower temperatures, the spectra of all complexes should be obtained at both room temperature and liquid nitrogen temperature in order to observe the effect of low temperature upon the spectra in the crystalline state. Wherever solubilities permit, the spectra should also be observed in solution as an aid in the assignment of any crystal lattice vibrations which may further complicate the solid state spectra. All applicable methods of sampling should be used to

eliminate the possibility of misinterpreting the KBr pellet spectra due to reaction or exchange of the elements present in the KBr window with the matrix. Procedures should be determined for the preparation of the deuterated hydrates. Integrated proton nuclear magnetic resonance spectra should be determined for all applicable materials as a further check on the quantitative number of coordinated water molecules existing per molecule of acetate. All applicable techniques of sample preparation should be used in both the sodium chloride and cesium bromide regions in order to learn as much as possible concerning the vibrations of these compounds. The absorptions due to the coordinated water molecules should be an excellent aid in determining the nature of the metal-ligand bonds. An attempt will also be made to differentiate between ionic and covalent bonding in the complexes studied. In a few of these compounds, X-ray diffraction work by other investigators has been published and in the cases where this work is available, the X-ray determinations will be compared with the results of the infrared data presented here in a further attempt to determine as much information as possible concerning the structures of these complexes. The X-ray and infrared studies will be discussed and compared in the hope of assigning a definite structure wherever possible. All spectra will be compared and similarities and differences will be explained from the point of view of coordination and hydrogen bonding.

PART II  
EXPERIMENTAL

A. Materials

1. Metallic Acetates. The acetates were obtained commercially in the purest form available. In most cases these were high purity reagent grade chemicals. C.P. grade chemicals were used when reagent grade materials were not available. All C.P. chemicals were further purified by recrystallization from distilled water and were dried over Drierite in a vacuum desiccator. A further check on the purity of the acetates was obtained by comparing the infrared and proton NMR spectra of the same acetate when it was available from more than one chemical supplier. This procedure was used wherever possible as a precaution against a possible mislabeling of the original acetate by the supplier. The metallic acetates are available commercially as either the normal hydrate, if the hydrate form is stable, or as the anhydrous acetate. In the case of sodium acetate, however, the trihydrate and the anhydrous compound are commercially available as reagent grade chemicals. Table I summarizes the source and purity of normally occurring anhydrous acetates and Table II gives this data for the acetates used here that are commercially available as hydrates.

Table I

## Source of Anhydrous Acetates

Anhydrous Acetate	Formula	Formula Weight	Origin Lot No.	Purity %
Barium Acetate	$\text{Ba}(\text{CH}_3\text{COO})_2$	255.452	Baker Reagent Lot No. 28083	99.3
Mercuric Acetate	$\text{Hg}(\text{CH}_3\text{COO})_2$	318.702	Baker Reagent Lot No. 23002	99.4
Potassium Acetate	$\text{CH}_3\text{COOK}$	98.146	Baker Reagent Lot No. 28185	100.0
Silver Acetate	$\text{CH}_3\text{COOAg}$	166.926	Baker Purified Lot No. 25287	...
Sodium Acetate	$\text{CH}_3\text{COONa}$	82.037	Baker Reagent Lot No. 25155	99.6
Thallous Acetate	$\text{CH}_3\text{COOTl}$	263.436	Fisher Purified Lot No. 724599	...

Table II

## Source of Hydrated Acetates

Hydrated Acetate	Formula	Formula Weight	Origin Lot No.	Purity %
Aluminum Subacetate	$\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	180.09	Fisher Purified Lot No. 713656	....
Cadmium Acetate	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	266.534	Baker Reagent Lot No. 20509	99.9
Calcium Acetate	$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	176.188	Baker Reagent Lot No. 28338	99.7
Chromic Acetate	$\text{Cr}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$	247.16	Fisher Reagent .....	99.9
Cobalt Acetate	$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	249.096	Baker Reagent Lot No. 28198	99.9
Cupric Acetate	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	199.648	Baker Reagent Lot No. 24403	99.5
Lead Acetate	$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	379.35	Baker Reagent Lot No. 24144	101.0
Lithium Acetate	$\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$	102.02	Fisher Purified Lot No. 720259	....
Magnesium Acetate	$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	214.476	Baker Reagent Lot No. 24113	99.6
Manganese Acetate	$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	245.096	Fisher Reagent Lot No. 713617	99.9
Nickel Acetate	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	248.866	Baker Reagent Lot No. 25159	99.8
Sodium Acetate	$\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$	136.085	Baker Reagent Lot No. 25068	101.0
Strontium Acetate	$\text{Sr}(\text{CH}_3\text{COO})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	214.73	Baker Reagent Lot No. 51447	99.7
Thorium Acetate	$\text{Th}(\text{OH})_2(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	402.244	Elmer & Amend Purified	....
Zinc Acetate	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	219.504	Baker Reagent Lot No. 25223	99.9

2. Deuterium Oxide. 99.7% deuterium oxide, supplied by the Liquid Carbonic Division of General Dynamics Corporation, was used in the preparation of the deuterated hydrates and as a solvent for the proton nuclear magnetic resonance spectra. It was shipped and stored in 100 c.c. sealed glass ampules. After opening a sealed ampule for use, the  $D_2O$  was transferred to a clean dry bottle with ground glass stopper and stored over Drierite in a desiccator.

3. Potassium Bromide. The potassium bromide used as a matrix for the pellet technique was powdered infrared quality obtained from the Harshaw Chemical Company (Lot Nos. 6890 and 9921).

4. Methanol. The methanol used as a solvent for the acetates in the deposited powder film technique was Fisher Certified Reagent of "Spectranalyzed Purity".

#### B. Methods

1. Preparation of Anhydrous Acetates. From the observation of Tables I and II, it can be seen that some acetates do not form stable hydrates at room temperature and are therefore available only as the anhydrous compounds. It is also shown, however, that the majority of acetates studied here were obtained commercially as hydrates. It was desired to



dehydrate these acetates so that the spectra of the anhydrous and hydrated species could be compared. Although each of these hydrates loses its water at a specific temperature, it was found that all could be satisfactorily dehydrated by heating the normal hydrate at 110 to 150 degrees Centigrade for one week. Dehydration was performed in 1 gram quantities by heating 1 gram of the normal hydrate in a weighing bottle without cover. At the end of one week of heating the covers were placed on the weighing bottles which were quickly removed to a desiccator containing Drierite. Dehydration was confirmed by the disappearance of  $\text{H}_2\text{O}$  stretching vibrations in the  $3700\text{--}3000\text{ cm.}^{-1}$  region, and by the absence of a water peak in the proton NMR spectra.

2. Preparation of Deuterated Hydrates. In the acetates studied, wherever normal hydrates occur, deuterated hydrates were prepared to show the effect of isotopic substitution upon the infrared spectra. The deuterated hydrates were prepared by placing approximately 0.5 grams of the normally hydrated crystals in 10 c.c. of 99.7%  $\text{D}_2\text{O}$  in a 15 c.c. bottle with ground glass stopper. In most cases the crystals dissolved completely. The stopper was tightly inserted and the bottle shaken and then placed over Drierite in a desiccator for about 12 hours. At the end of this time period, the stopper was removed and the bottle and contents quickly placed over Drierite in a vacuum desiccator connected to a vacuum pump with a cold

trap inserted in the line. The pumping was continued until all the solution was removed. Then 10 c.c. of fresh  $D_2O$  were added to the crystals in the bottle and the stopper inserted and the bottle shaken and placed in the desiccator for another 12 hours. This exact procedure was repeated with approximately 10 fresh fillings with  $D_2O$  for each sample or until the infrared spectra showed at least 90% deuterated hydrate present. The same procedure was used to prepare all the deuterated hydrates. Once prepared, the deuterated hydrates were stored in tightly stoppered bottles over Drierite in a desiccator so that they would not revert to the normal hydrated form by reverse exchange with the water vapor present in the atmosphere.

### 3. Infrared Absorbance Measurements

a. Instruments. Infrared spectra were obtained with a Perkin-Elmer Model 421 Double Beam Recording Spectrophotometer equipped with a Dual-Grating Interchange for the 4000 to  $550\text{ cm}^{-1}$  region and with a Cesium Bromide Interchange for the 600 to  $250\text{ cm}^{-1}$  region. Spectra were also recorded with a Perkin-Elmer Model 221 Recording Spectrophotometer equipped with a Prism-Grating Interchange for the 4000 to  $600\text{ cm}^{-1}$  region and with the Cesium Bromide Interchange for the far infrared region. A Perkin-Elmer Model 21 spectrophotometer and an Infracord instrument, equipped with rock salt optics, were used to a lesser extent. All spectra were finally obtained using

the Model 421 instrument for the sake of comparison since this instrument records linearly in wavenumbers and possesses greater resolution than the others. The Cesium Bromide Interchange, however, records linearly in microns and all absorption bands obtained using it have been converted to wavenumbers for standardization purposes. The Model 421 spectrophotometer, used extensively in this research, was calibrated using the absorption bands of polystyrene, and  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{HCl}$  and  $\text{CH}_4$  vapors. Calibration was continually checked to insure an accuracy of  $\pm 1 \text{ cm}^{-1}$ .

b. Infrared sampling techniques. Infrared spectra of the acetates studied were obtained using the following sampling methods; solution in  $\text{D}_2\text{O}$ , Nujol mull, deposited powder film, and the KBr pellet technique. KBr pellet spectra were found to agree with the mull spectra showing that there is no apparent interaction of these compounds with the KBr matrix. The concentration of sample in KBr was approximately 1% but in cases was varied from approximately 0.5 to 3% in order to accurately determine the positions of weak or strong bands, respectively. The aim of this study was not "absolute intensity" measurements. Blank KBr pellets contain some water and give rise to a broad absorption at approximately  $3400 \text{ cm}^{-1}$ . For this reason a small water band occurs in the spectra of the

anhydrous, dehydrated, and deuterated acetates.

c. Low temperature analysis. Low temperature spectra were obtained using two specially designed cells, one with sodium chloride windows for the 4000 to 600  $\text{cm}^{-1}$  region and the other with cesium bromide windows for the 600 to 250  $\text{cm}^{-1}$  region. These cells were used to obtain the spectra of the acetates at liquid nitrogen temperature as KBr pellets and as powder films deposited from spectroscopic grade methanol on NaCl windows. The cells were loaded at room temperature and connected to a vacuum rack by means of a "snake" and pumped out until the pressure in the cell was approximately  $10^{-6}$  mm. Hg. The cells were then removed from the vacuum rack and the spectra scanned at room temperature. Next, the cells were reattached to the rack and liquid nitrogen poured into the coolant well. The liquid nitrogen boiled away vigorously at first, but as the copper cooled less liquid nitrogen was needed to maintain a satisfactory level in the coolant well. The cells were left attached to the rack and the level of liquid nitrogen maintained for 30 to 45 minutes. The cells were then removed from the rack and the infrared spectra of the samples recorded at liquid nitrogen temperature with the coolant level being maintained. Although a thermocouple was not used to measure the temperature exactly, it is believed that the actual temperature of the cells

closely approaches liquid nitrogen temperature when the above procedure is followed. A diagram of the sodium chloride low temperature cell is given in Figure 1. The cell was used with NaCl windows for the 2 to 15 micron region and a similar cell, with a smaller distance between windows, was used with CsBr windows for the 14 to 40 micron region. Low temperature spectra were recorded using these cells in their appropriate regions for all the anhydrous, hydrated and deuterated salts.

d. Solution measurements. Spectra of the acetates were observed in  $D_2O$  solution using an 0.015 mm Irtran liquid cell in the  $4000$  to  $700\text{ cm}^{-1}$  region. The cell was obtained from the Connecticut Instrument Company and the actual thickness was calculated to be 0.01452 mm using the interference fringe method. This cell was used in an effort to locate any crystal lattice vibrations which might further complicate the solid state spectra.  $D_2O$  was chosen as the solvent for this analysis because of the limited solubility of the acetates in other solvents and because the undeuterated acetates have no absorption in the region where  $D_2O$  absorbs. Irtran windows are completely resistant to aqueous solutions of these acetates.

#### 4. Proton NMR Measurements

a. Equipment. Proton nuclear magnetic resonance spectra were obtained using a Varian Associates A-60 NMR

Figure 1  
Sodium Chloride Low Temperature Cell

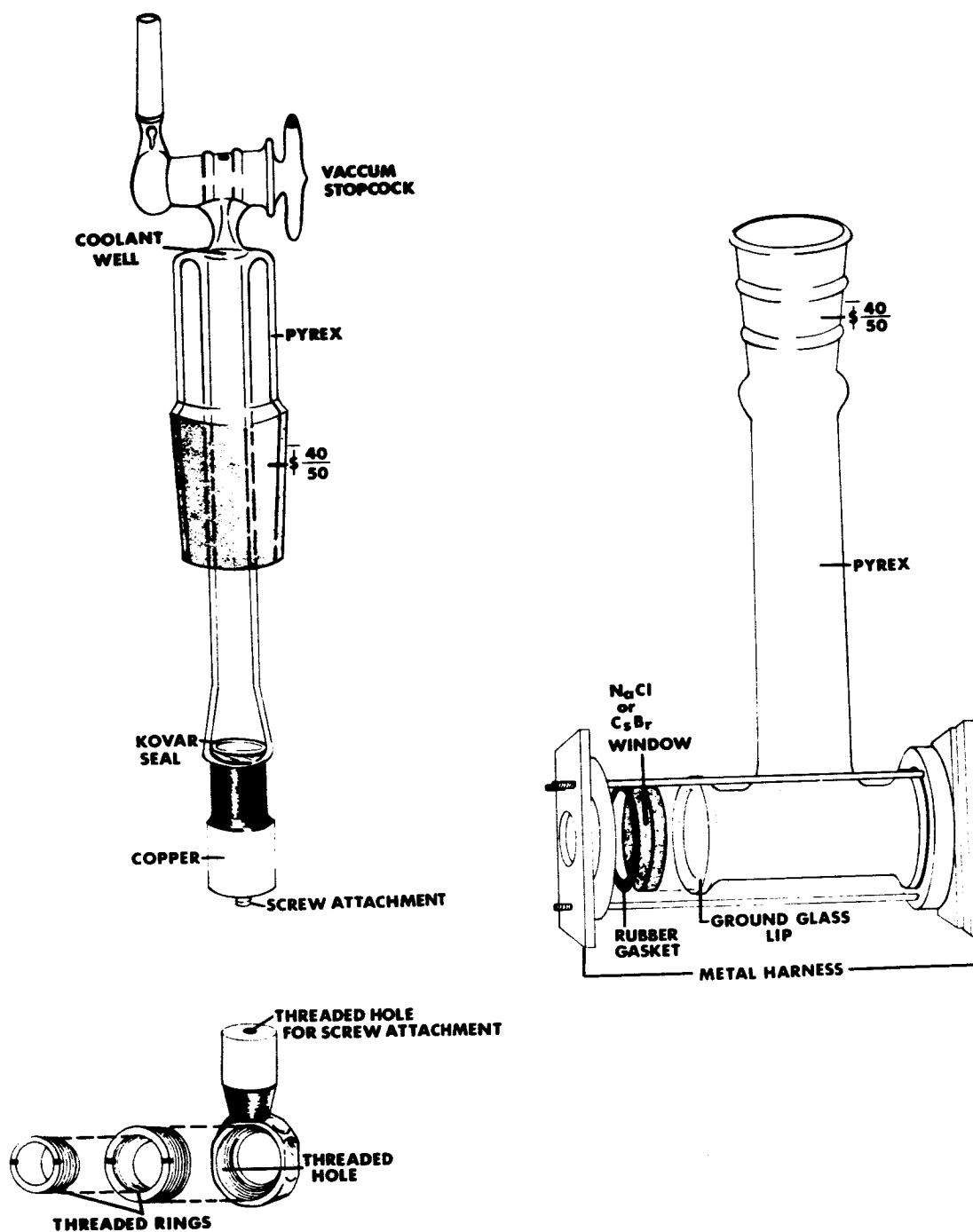


FIGURE I

Spectrometer with a variable temperature probe. The instrument was calibrated using a sealed Varian sample tube containing 50% chloroform and 50% tetramethylsilane.

b. Spectral measurements. Proton NMR spectra of the acetates were obtained at 33-37 degrees Centigrade as 20% solutions in 99.7%  $D_2O$  using Varian sample tubes with capillary tetramethylsilane as a reference standard. Integrals were obtained for the hydrates comparing the area of the  $H_2O$  peak with the  $CH_3$  peak in order to further substantiate the number of coordinated water molecules existing per molecule of acetate. Excellent NMR spectra were obtained for all the compounds with the exception of those containing paramagnetic metals. Blanks were continually observed to be certain that the  $D_2O$  was of high purity and that it was not contaminated with ordinary water.



## PART III

## RESULTS AND DISCUSSION

Water vapor exhibits asymmetric and symmetric stretching vibrations at 3756 and 3652  $\text{cm}^{-1}$  respectively and bending vibrations at 1595  $\text{cm}^{-1}$ . Coordinated water absorptions should not differ greatly from that of the vapor provided that the metal-oxygen bond is essentially ionic. If the metal-oxygen bond is covalent, however, absorptions such as wagging, twisting, and rocking modes characteristic of coordinated water should be activated.<sup>18</sup>

A. Tetrahydrate Acetates

1. X-ray Diffraction Data. From the X-ray analysis of nickel acetate  $\cdot 4\text{H}_2\text{O}$  and cobalt acetate  $\cdot 4\text{H}_2\text{O}$ <sup>78</sup> and magnesium acetate  $\cdot 4\text{H}_2\text{O}$ <sup>67</sup> space group and the monoclinic unit cell dimensions are tabulated in Table III and bond lengths and angles for cobalt and nickel tetrahydrate acetates are presented in Table IV.

Table III

X-ray Data for Nickel, Cobalt and Magnesium Tetrahydrate Acetates

	Space Group	Unit Cell Dimensions*				Formula Units per Unit Cell
		a	b	c	$\beta$	
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	$\text{P2}_1/\text{c}$	4.75	11.77	8.44	$93^\circ 36'$	2
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	$\text{P2}_1/\text{c}$	4.77	11.85	8.42	$94^\circ 30'$	2
$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	$\text{C}_{2h}^2\text{-P2}_1/\text{m}$	8.3	11.7	4.7	$94.9^\circ$	2

\* in Angstroms

Table IV

Bond Lengths and Angles  
Cobalt and Nickel Tetrahydrate Acetates

Ni-O or Co-O	2.12A
Ni-H <sub>2</sub> O or Co-H <sub>2</sub> O (in plane)	2.11A
Ni-H <sub>2</sub> O or Co-H <sub>2</sub> O (out of plane)	2.06A
Acetate O-O	2.27A
Acetate C-O (bonded to metal)	1.29A
Acetate C-O (H bonded to water)	1.31A
C-C	1.56A
O-Ni-H <sub>2</sub> O (in plane) or O-Co-H <sub>2</sub> O (in plane)	90°44'
O-Ni-H <sub>2</sub> O (out of plane) or O-Co-H <sub>2</sub> O (out of plane)	90°33'
H <sub>2</sub> O (in plane)-Ni-H <sub>2</sub> O (out of plane) or H <sub>2</sub> O (in plane)-Co-H <sub>2</sub> O (out of plane)	88°30'
Acetate O-C-O (Acetate)	121°39'

Hydrogen Bonds

O-H <sub>2</sub> O (out of plane)	2.59A (Intramolecular)
O-H <sub>2</sub> O (in plane)	2.66A (Intramolecular)
O-H <sub>2</sub> O (in plane)	2.64A (Intermolecular)
H <sub>2</sub> O (in plane)-O	2.64A (Intermolecular)

Nickel and cobalt tetrahydrate acetates are shown to be isostructural from the X-ray data while magnesium acetate .4H<sub>2</sub>O has a similar structure. X-ray diffraction data is not available for manganese acetate .4H<sub>2</sub>O.

a. Structure of nickel and cobalt acetates  $\cdot 4\text{H}_2\text{O}$ .

van Niekerk and Schoening<sup>78</sup> describe the structure of nickel or cobalt tetrahydrate acetates by stating that each nickel or cobalt atom is surrounded octahedrally by four water molecules and by two oxygen atoms which belong to two different acetate groups. The remaining oxygen atom of an acetate group is linked by a hydrogen bond of length 2.59A to a water molecule within the same nickel coordination group. The two acetate groups and the four water molecules which constitute the nearest neighbors of a metal atom are further linked by hydrogen bonds to similar groups surrounding other metal atoms in the structure. The way in which this is accomplished is as follows: one water molecule belonging to the group makes one hydrogen bond of 2.66A to the oxygen atom of an acetate group bonded to the metal and also a second hydrogen bond of length 2.64A to the oxygen atom of an adjacent acetate group in the structure. Within their experimental error, the acetate groups were found to be separately planar.

b. Bonding in nickel and cobalt acetates  $\cdot 4\text{H}_2\text{O}$ .

van Niekerk and Schoening show that the bond distances between the nickel atom and the four water molecules (2.11 and 2.06A) and between the nickel atom and the two oxygen atoms (2.12A) in the nickel acetate structure can be compared with similar distances in other octahedrally coordinated nickel structures.

Thus in  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  the nickel-water distances are 2.02 and 2.04A and in  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  they vary between 1.95 and 2.13A. As is the case in other hydrated nickel salts, the nickel-water and nickel-oxygen bonds in this structure are probably mainly ionic in character.

In cobalt acetate  $\cdot 4\text{H}_2\text{O}$ , the cobalt-water (2.11 and 2.06A) and cobalt-oxygen (2.12A) distances seem to indicate essentially ionic bonds, as will be seen when comparing these distances with the calculated 1.98A covalent bond length and the calculated 2.12A ionic bond length for cobalt structures. One oxygen atom of an acetate group is linked by two hydrogen bonds to two water molecules, while the other oxygen atom makes one hydrogen bond to a water molecule and also an ionic bond to the doubly positive metal ion. The influence of these bonds on the two oxygen atoms of an acetate group may be equal, thus accounting for the equal lengths of the oxygen-carbon bonds.

This discussion can be clarified by referring to Figure 2 which basically represents the structure of nickel or cobalt tetrahydrate acetates and to Figure 3 which more accurately represents the structures. Dotted lines are used to represent hydrogen bonding which is a very important factor in the stability of these compounds. Since cobalt and nickel acetates  $\cdot 4\text{H}_2\text{O}$  are isostructural, bond lengths and angles and descriptions of the structure are applicable to either.

Figure 2  
Basic Structure of Nickel and Cobalt  
Tetrahydrate Acetates.

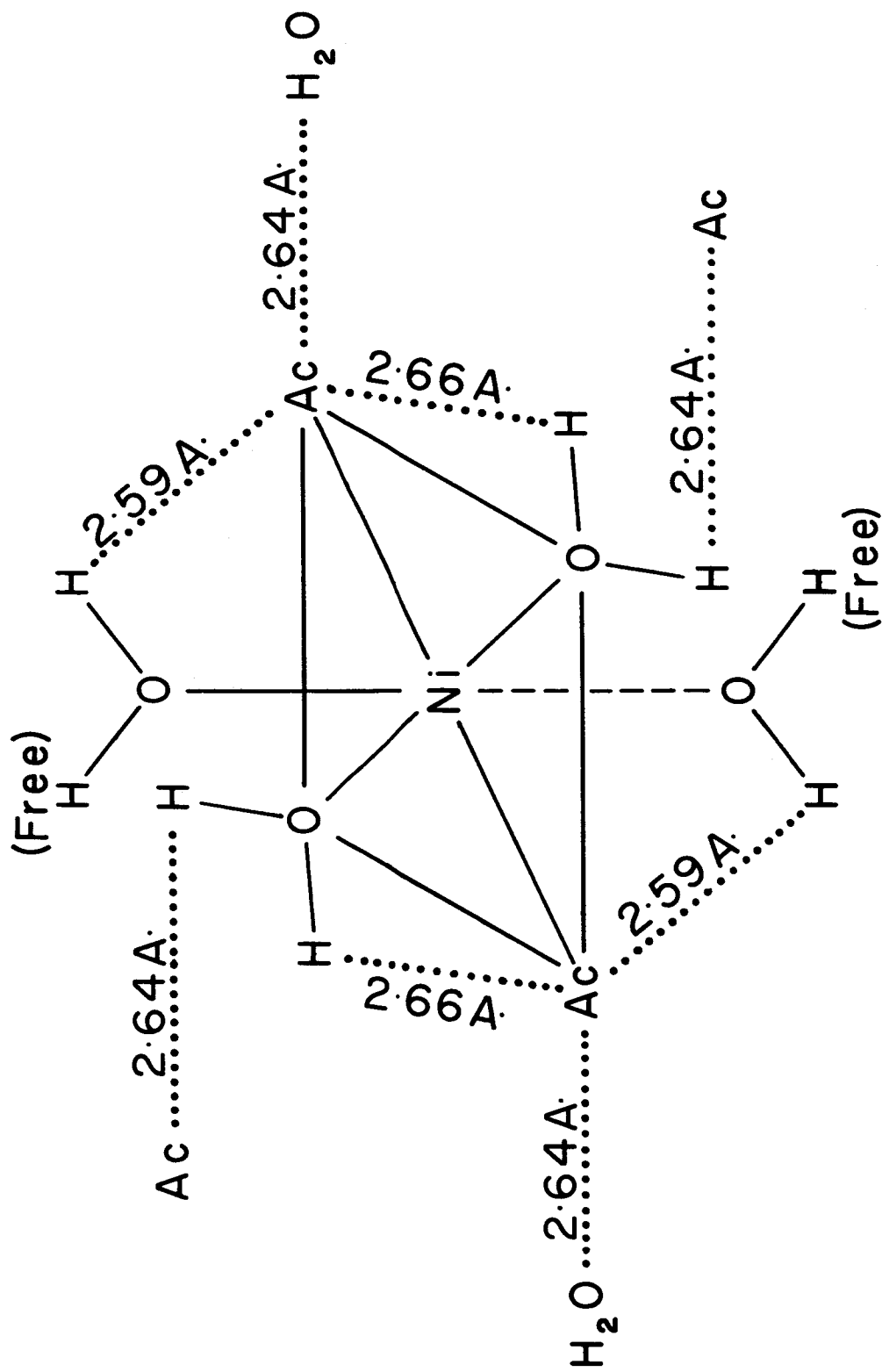
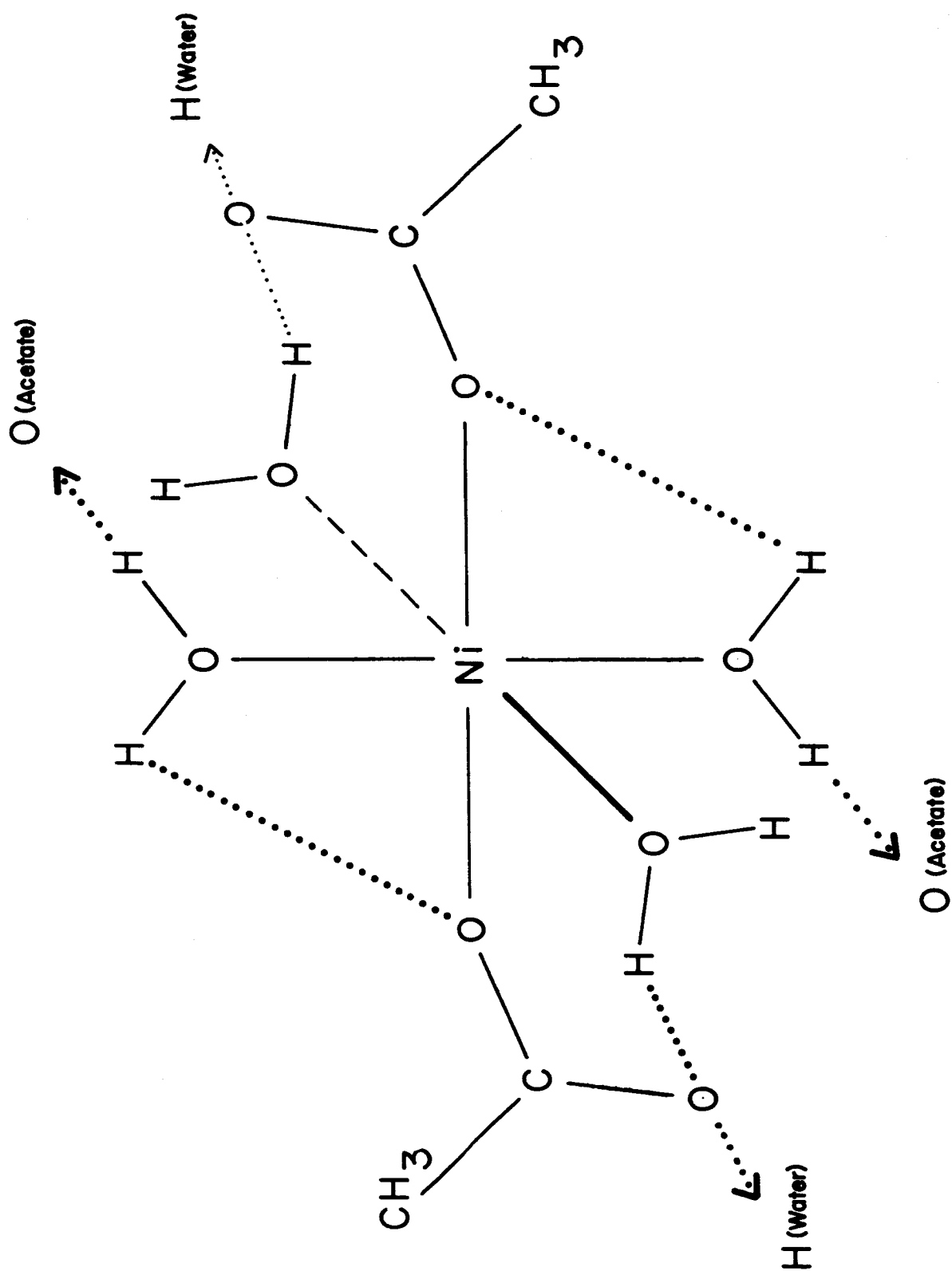


Figure 3  
Structure of Nickel  
and Cobalt Tetrahydrate Acetates





From examination of Figure 3 it can be seen that although there are four water molecules bonded to the metal atom, they are not all exactly equivalent. One pair of the water molecules is seen to be equivalent by having all their protons involved in hydrogen bonding. One proton of each water molecule forms a hydrogen bond (2.66A) within the same molecule (intramolecular) to the oxygen atom of an acetate group which is bonded to the metal. The other protons of these two water molecules form hydrogen bonds (2.64A) to adjacent oxygen atoms of acetate groups, not bonded to the metal, of the next molecule in the structure (intermolecular). Thus this pair of water molecules coordinated to the metal atom gives rise to the formation of intra- and inter-molecular hydrogen bonds.

The remaining pair of water molecules are equivalent and are seen to give rise to only one intramolecular hydrogen bond (2.59A) each to the oxygen atom of the acetate group within the same molecule that is not bonded to the central metal atom. The other proton of each of these water molecules is not sufficiently close to any negative charge and does not form any appreciable hydrogen bond in the three dimensional crystal lattice. These two protons are thus essentially free and should appear as such in the infrared spectra of nickel, cobalt, and magnesium tetrahydrate acetates.

## 2. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Room Temperature (4000-250 $\text{cm}^{-1}$ )

a. Nickel, cobalt, and magnesium acetates. Nickel, cobalt, and magnesium tetrahydrate acetates each exhibit a fairly sharp absorption at  $3475\text{--}3527\text{ cm}^{-1}$  and a broad absorption at  $3150\text{--}3180\text{ cm}^{-1}$  at room temperature as shown in Figure 4. These bands retain their form but shift to  $2576\text{--}2615\text{ cm}^{-1}$  and  $2233\text{--}2390\text{ cm}^{-1}$  respectively upon exchange of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  as the coordination water as shown in Figure 5, and disappear completely from the spectra upon dehydration. These absorptions are characteristic of the coordinated water in these complexes. The sharp band at  $3475\text{--}3527\text{ cm}^{-1}$  is assigned as the  $\text{H}_2\text{O}$  stretching vibration of the free water protons that do not form hydrogen bonds. The very broad absorption at  $3150\text{--}3180\text{ cm}^{-1}$  is assigned as the  $\text{H}_2\text{O}$  stretching vibration of the remaining hydrogen bonded water protons. Since there are hydrogen bonded protons of different bond lengths and also inter- and intra-molecular hydrogen bonds present, it should be possible, with a high resolution spectrophotometer, to observe the splitting of this broad band into distinct peaks characteristic of the type of hydrogen bonded protons present. This phenomena may occur in some cases at room temperature and should be readily visible at liquid nitrogen temperature.

Nickel, cobalt, and magnesium tetrahydrate acetates

Figure 4

Infrared Spectra of Nickel, Cobalt, and Magnesium  
Tetrahydrate Acetates in the Region ( $3000-3700\text{ cm}^{-1}$ )

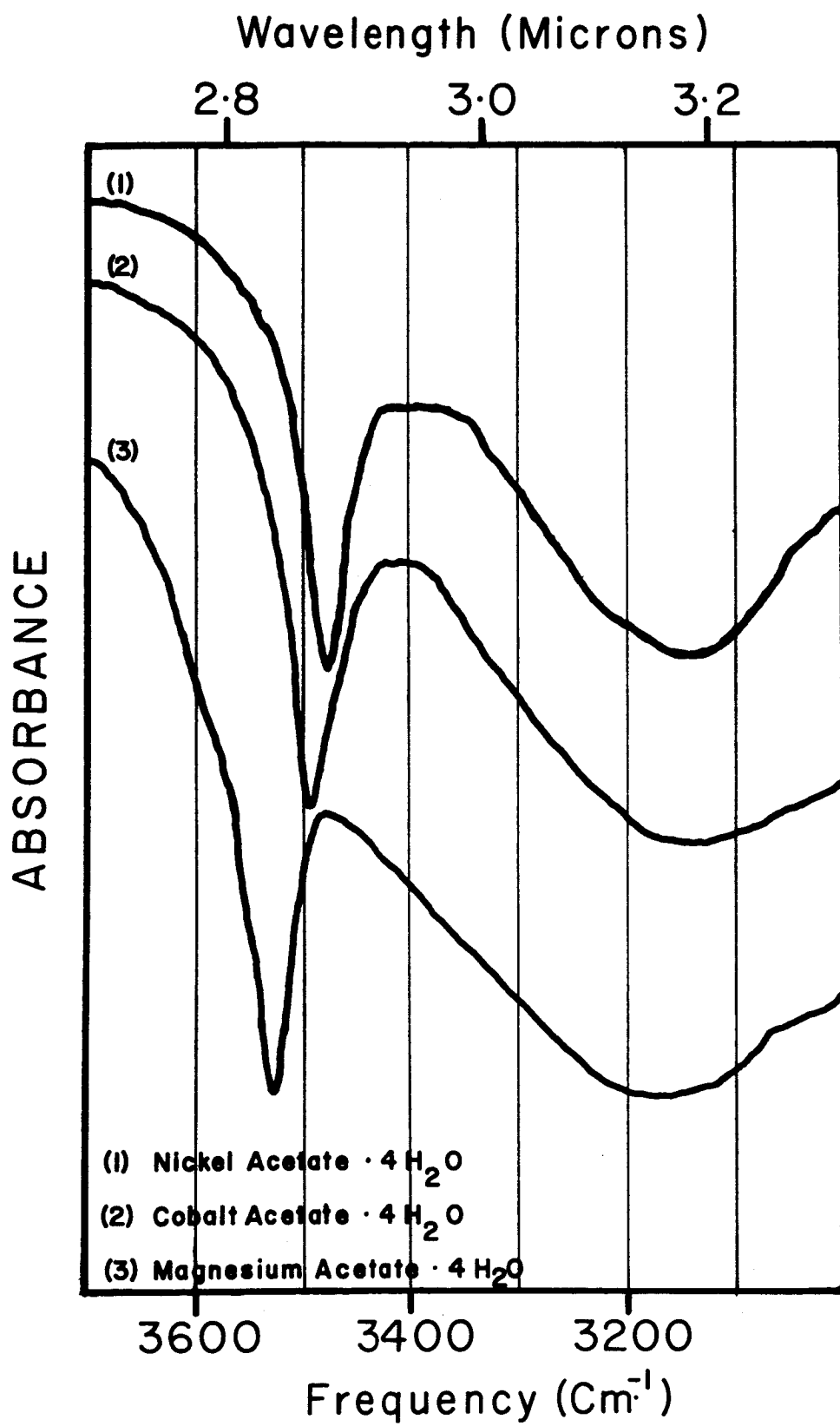
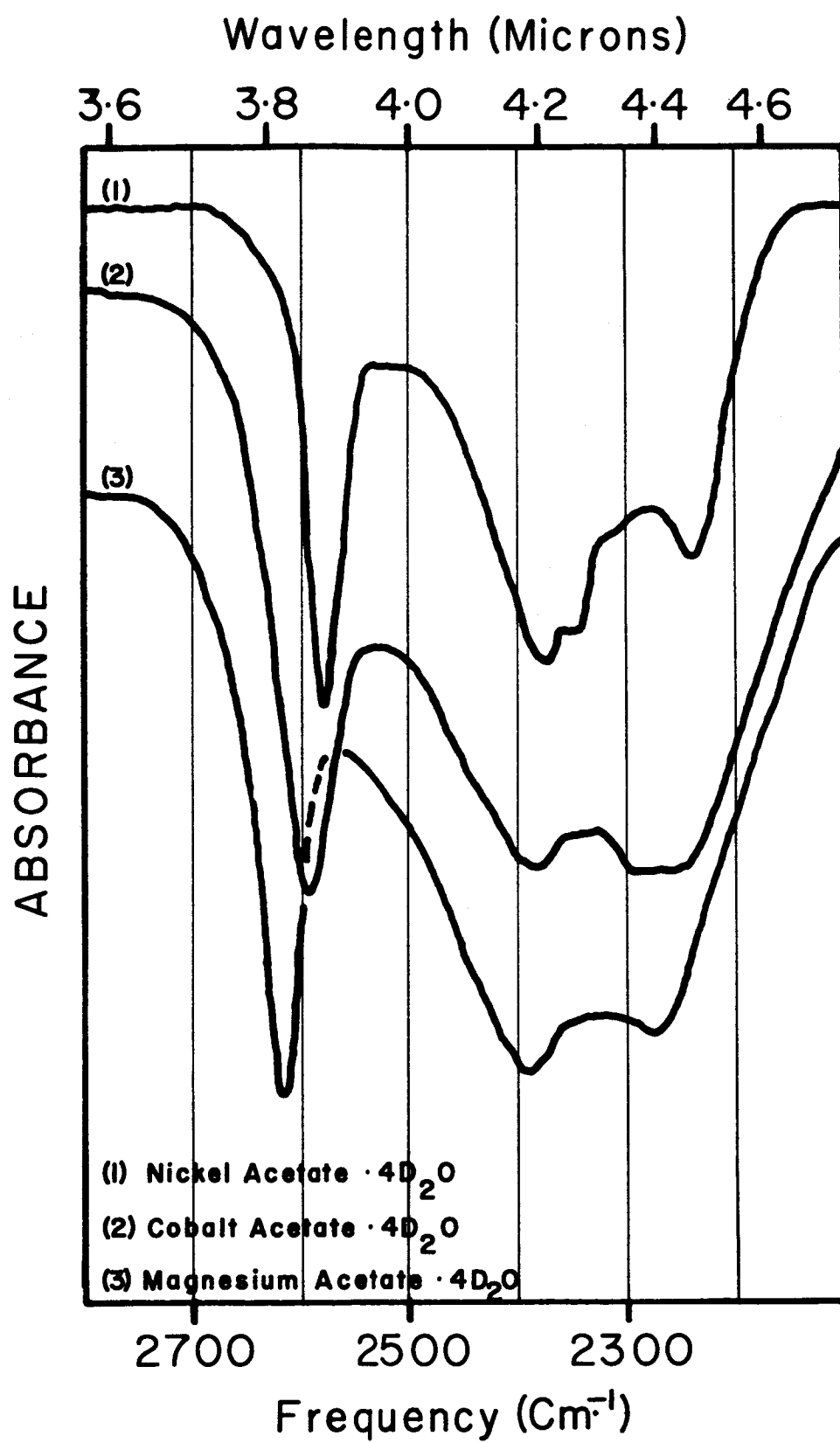


Figure 5  
Infrared Spectra of Nickel, Cobalt, and Magnesium  
Acetates .4D<sub>2</sub>O in the Region (2100-2800 cm.<sup>-1</sup>)



give rise to an absorption at  $1690\text{--}1708\text{ cm}^{-1}$  which shifts to  $1150\text{--}1165\text{ cm}^{-1}$  upon exchange of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  and disappears upon dehydration and can be assigned as the  $\text{H}_2\text{O}$  bending vibration of the coordinated water molecules.

These hydrated acetates also have absorptions at  $856\text{--}904\text{ cm}^{-1}$ ,  $803\text{--}813\text{ cm}^{-1}$ , and  $724\text{--}745\text{ cm}^{-1}$  as shown in Figure 6. These absorptions disappear from the spectra upon dehydration as presented in Figure 7, and shift upon formation of the deuterated hydrate as can be seen from Figure 8 which compares the spectra of nickel acetate  $\cdot 4\text{H}_2\text{O}$  with the dehydrated and deuterated compounds. These absorptions are assigned to wagging, twisting, or rocking modes of the coordinated water molecules. As stated previously, these absorptions can only be activated provided that there is some covalent character attached to the metal-water bonds.

Table VI, Table VII and Table VIII give the complete infrared spectral bands in the  $4000\text{--}250\text{ cm}^{-1}$  region for nickel, cobalt and magnesium tetrahydrate acetates respectively. Included also are the complete spectra of the dehydrated and deuterated compounds for comparison. Band assignments are obtained by referring to Table V, which is the key to all absorption band assignments of the acetates studied.

Abbreviations for band intensities (I) found in the complete spectral tables are as follows:

vw - very weak	b - broad
w - weak	sh - shoulder
m - medium	s - strong
vs - very strong	

Figure 6  
Infrared Spectra of Nickel, Cobalt, and Magnesium  
Acetates  $\cdot 4\text{H}_2\text{O}$  in the Region  $(600-1200\text{ cm}^{-1})$



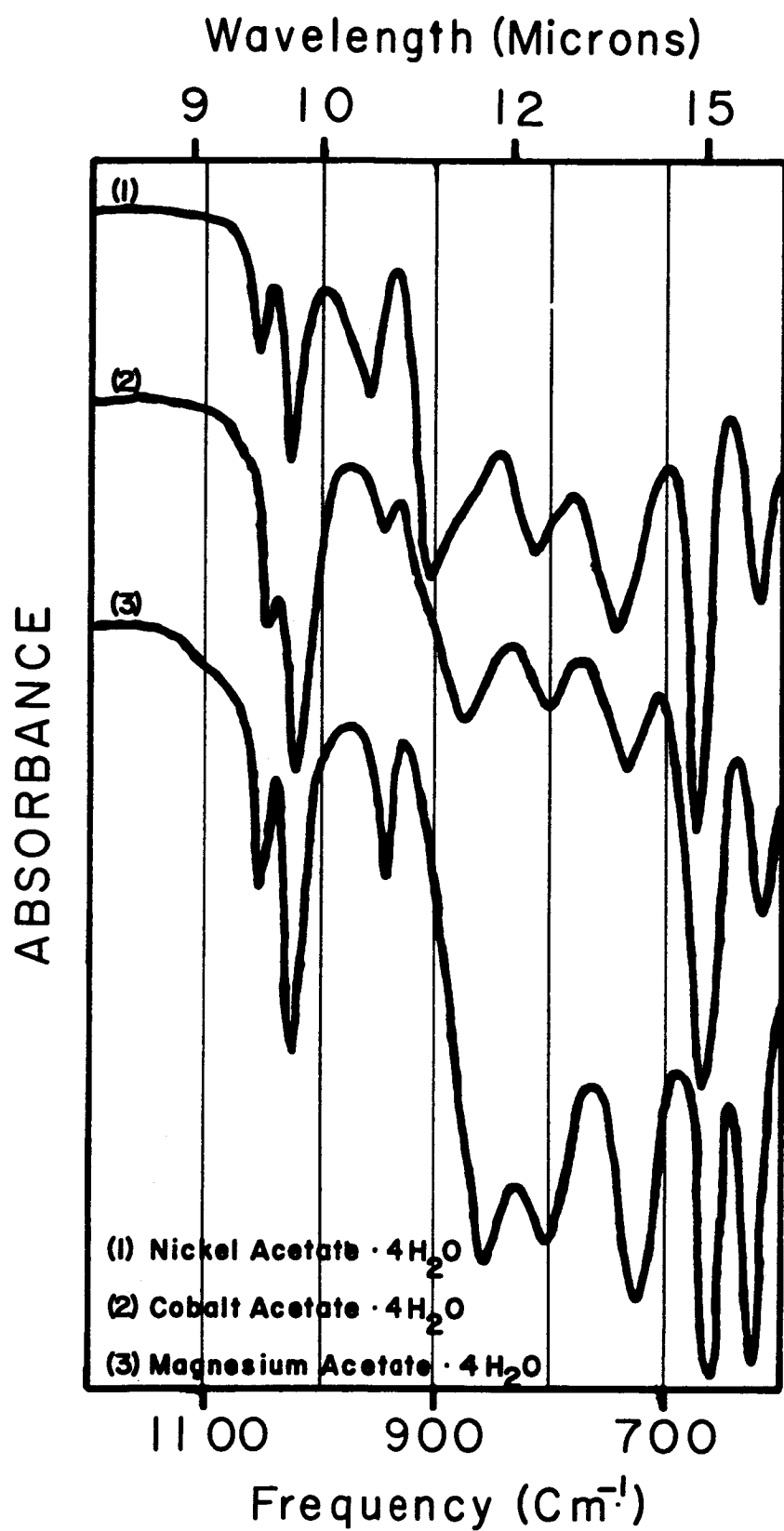


Figure 7  
Infrared Spectra of Nickel, Cobalt, and Magnesium  
Acetates Dehyd. in the Region (600-1200  $\text{cm}^{-1}$ )

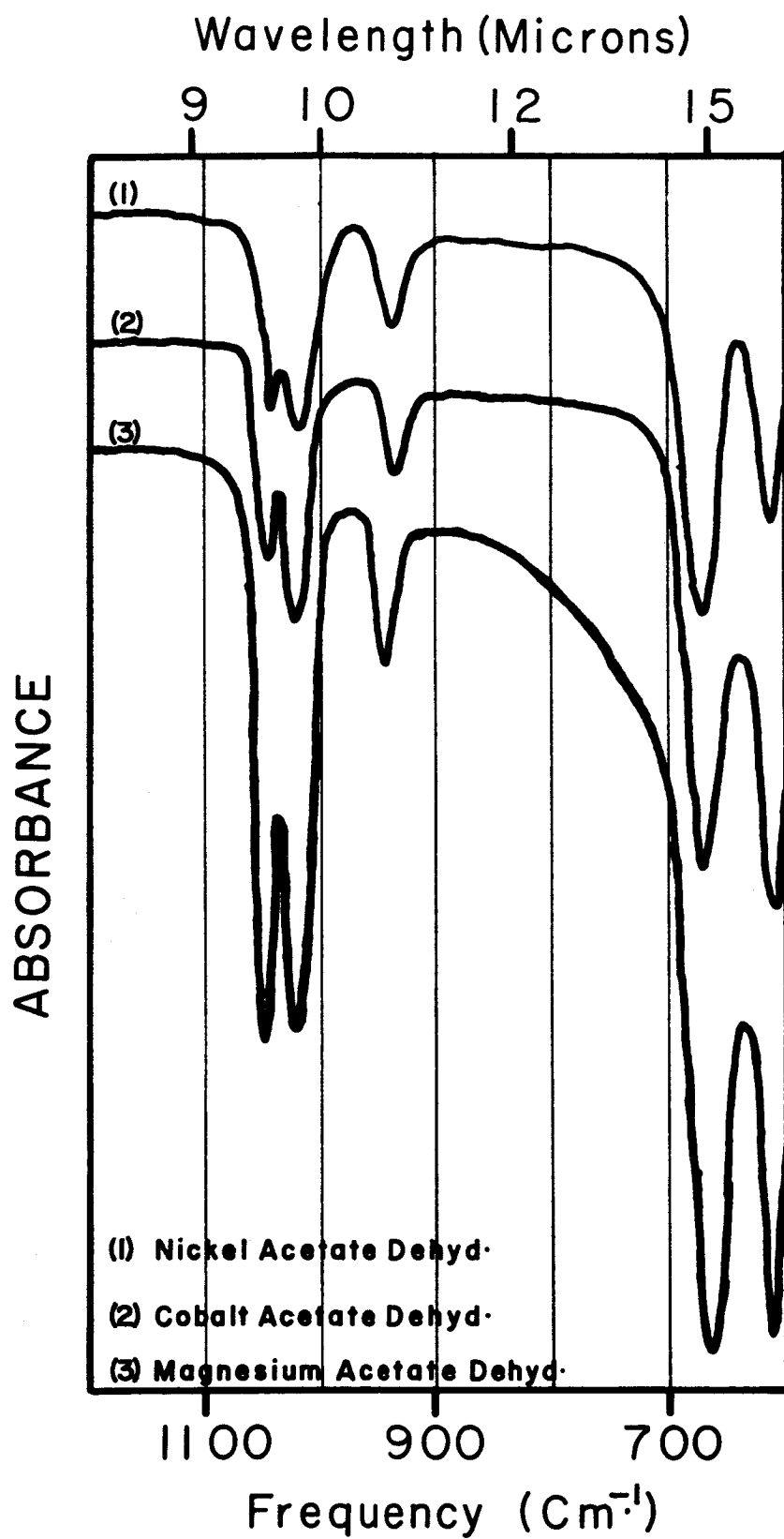
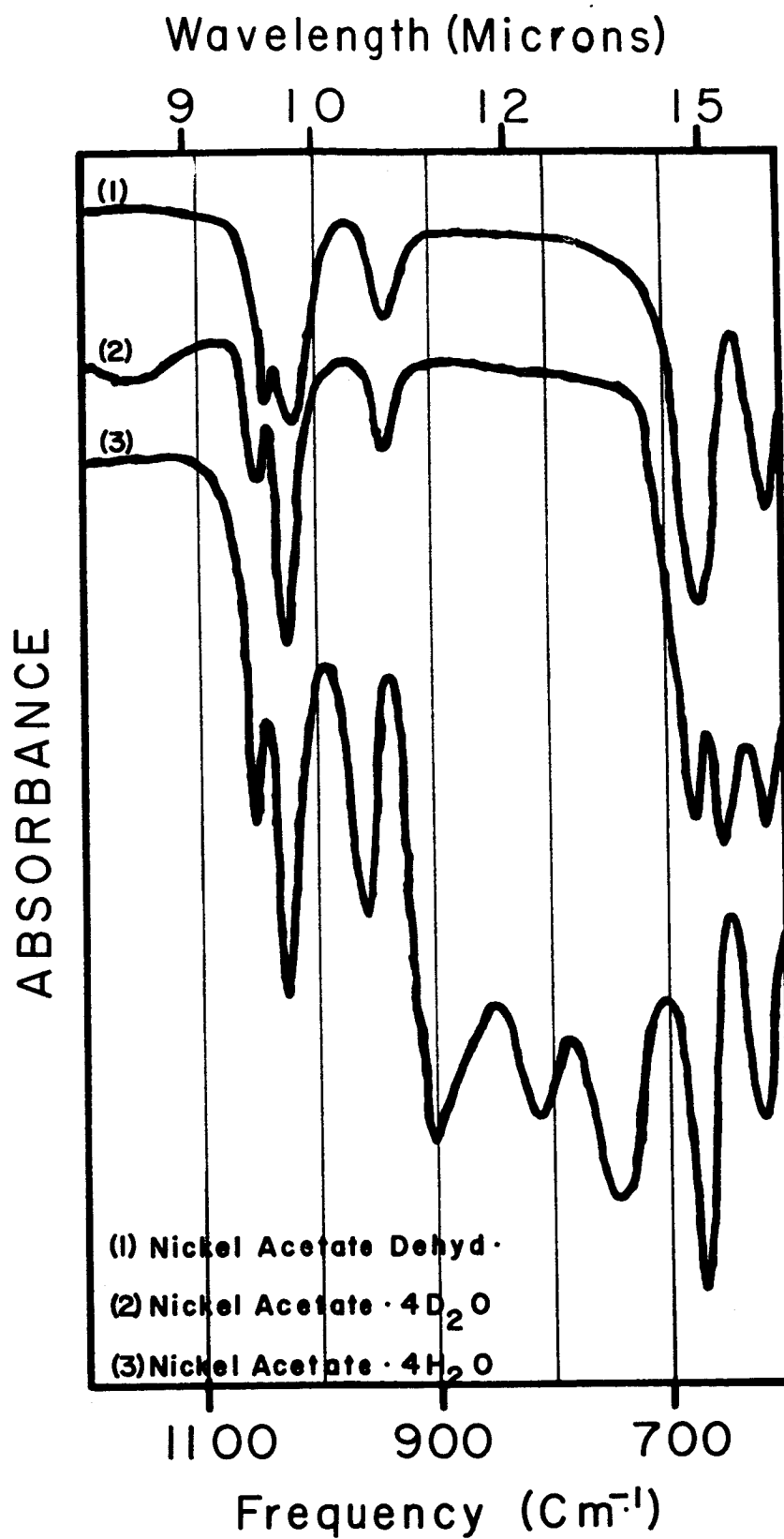


Figure 8  
Infrared Spectra of Nickel Acetate Dehyd.,  
.4D<sub>2</sub>O and .4H<sub>2</sub>O in the Region (600-1200 cm<sup>-1</sup>).



KEY TO ABSORPTION BAND ASSIGNMENTS

<u>Code</u>	<u>Assignment</u>
a .....	Free H <sub>2</sub> O stretching
b .....	Bonded H <sub>2</sub> O stretching
c .....	CH <sub>3</sub> asymmetrical stretching
d .....	CH <sub>3</sub> symmetrical stretching
e .....	Free D <sub>2</sub> O stretching
f .....	Bonded D <sub>2</sub> O stretching
g .....	H <sub>2</sub> O bending
h .....	CO <sub>2</sub> asymmetrical stretching
i .....	CH <sub>3</sub> asymmetrical bending
j .....	CO <sub>2</sub> symmetrical stretching
k .....	CH <sub>3</sub> symmetrical bending
l .....	D <sub>2</sub> O bending
m .....	D <sub>2</sub> O bending
n .....	CH <sub>3</sub> rocking
o .....	C-C stretching
p .....	H <sub>2</sub> O rocking, twisting, or wagging
q .....	H <sub>2</sub> O rocking, twisting, or wagging
r .....	H <sub>2</sub> O rocking, twisting, or wagging
s .....	CO <sub>2</sub> symmetrical bending
t .....	CO <sub>2</sub> rocking
u .....	D <sub>2</sub> O rocking, twisting, or wagging + H <sub>2</sub> O and D <sub>2</sub> O librational modes
v .....	Low energy acetate vibrations (libra- tional modes)
w .....	Free OD stretching
x .....	CO <sub>2</sub> rocking
y .....	Combination band (n + x)
z .....	Free OH stretching

Table VI

Infrared Absorption Bands of Nickel Acetate Dehyd.,  $.4\text{H}_2\text{O}$  &  $.4\text{D}_2\text{O}$ 

Nickel Acetate Dehyd.		Nickel Acetate $.4\text{H}_2\text{O}$		Nickel Acetate $.4\text{D}_2\text{O}$		ASSGN
Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	
		3475 s	3462 s			a
		3150 bs	3130 bs			b
3010 vw	3005 vw	3012 vw	3012 vw	3012 vw	3012 vw	c
2985 vw	2976 vw	2975 vw	2975 vw	2980 vw	2980 vw	c
2935 vw	2930 vw	2935 vw	2930 vw	2934 vw	2934 vw	d
				2576 s	2555 s	e
				2377 bs	2371 s	f
				2350 bs	2350 s	f
					2293 s	f
				2233 bs	2234 s	f
		1690 w				g
1564 s	1560 s	1541 s	1532 s	1550 s	1530 s	h
1442 s	1445 m	1450 m	1450 m	1451 s	1451 s	i
1418 s	1415 s	1423 s	1423 s	1424 s	1420 s	j
1341 m	1340 m	1349 m	1351 m	1351 m	1351 m	k
				1150 w	1155 w	l
					1112 vw	m
1045 w	1047 w	1054 w	1056 w	1053 w	1056 w	n
1025 m	1025 m	1028 m	1031 m	1026 m	1030 m	n
939 m	939 m	960 m	966 m	940 m	940 m	o
		904 m	910 m			p
			884 w			p
		813 m	826 m			q
		745 m	761 m			r
676 s	678 s	676 s	680 s		682 m	s
			646 m	653 s	663 sh	s
					651 s	u
615 m	614 m	623 m	620 m		628 s	t
				609 s	612 s	t
			599 s			u
		550 s	575 s	551 s	559 s	u
			506 vw			u
				465 m	482 m	u
					447 m	u
				421 w	432 s	u
				413 m		u
		383 m	396 s		394 m	u
					384 s	u
			359 s	377 w	376 sh	u
				370 m	353 sh	u
				339 w	347 s	u
				331 m		v
330 vw	327 vw	343 w				v
316 vw	317 vw	312 vw	312 vw		307 bm	v
300 vw	299 vw	302 w	306 m		299 bm	v
		294 w	296 w	296 m		v
282 vw	281 vw	284 vw	279 w	283 w	282 bm	v
275 vw	275 vw	276 w	272 vw	272 m	274 m	v
		269 vw				v

Table VII

Infrared Absorption Bands of Cobalt Acetate Dehyd.,  $.4\text{H}_2\text{O}$  and  $.4\text{D}_2\text{O}$ 

Cobalt Acetate Dehyd.		Cobalt Acetate $.4\text{H}_2\text{O}$		Cobalt Acetate $.4\text{D}_2\text{O}$		Assign.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3492 s	3487 s			a
		3150 bs	3120 bs			b
3010 vw	3006 vw	3010 vw	3010 vw	3010 vw	3010 vw	c
2985 vw	2980 vw	2985 vw	2985 vw	2985 vw	2983 vw	c
2934 vw	2928 vw	2932 vw	2932 vw	2934 vw	2934 vw	d
				2593 s	2570 s	e
				2380 bs	2380 s	f
				2270 bs	2270 s	f
		1700 w	1700 w			g
1562 bs	1570 bs	1551 bs	1520 bs	1545 bs	1545 s	h
	1448 s		1451 s		1445 s	i
1415 bs	1412 s	1418 bs	1418 s	1420 bs	1420 s	j
1338 m	1342 m	1343 m	1351 m	1350 m	1349 m	k
			1332 vw			
1044 w	1047 w	1050 w	1059 w	1155 bm	1156 m	m
1022 m	1022 m	1023 m	1032 m	1053 w	1055 w	n
935 w	938 w	946 w	951 w	1025 m	1025 m	n
		880 m	891 m	938 w	938 m	o
			869 m			p
		804 m	824 m			p
		736 m	756 m			q
						r
669 s	673 s	673 s	673 s		695 m	s
				669 s	678 s	s
610 m	612 m	621 m	625 m	631 bs	641 s	s
		532 bm	538 bs	607 bs	610 s	t
				535 m	555 s	u
					505 w	u
					473 s	u
				454 m	437 m	u
				402 m	421 s	u
		360 m			363 s	u
		352 vw		352 w		u
		348 vw		345 m		u
		343 w				u
		336 vw	335 bw	338 m	338 m	u
		331 vw		330 m		u
315 w	310 w	296 m	303 bm	318 w	312 vw	v
300 w	299 w	292 w	293 bw	296 m	297 w	v
282 w	282 w	275 m	276 bm	283 w	283 w	v
273 w	273 w	272 w	269 bw	271 m		v
		268 w			268 w	v



Table VIII

Infrared Absorption Bands of Magnesium Acetate Dehyd., .4H<sub>2</sub>O and .4D<sub>2</sub>O

Magnesium Acetate Dehyd		Magnesium Acetate.4H <sub>2</sub> O		Magnesium Acetate.4D <sub>2</sub> O		Assn
Room Temp cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3527 s	3498 s			a
		3180 bs	3170 s			b
			3100 s			b
3015 vw	3015 vw	3015 vw	3015 vw	3015 vw	3005 vw	c
2990 vw	2985 vw	2995 vw	2995 vw	2995 vw	2990 vw	c
2935 vw	2935 vw	2937 vw	2937 vw	2936 vw	2930 vw	d
				2615 s	2592 s	e
				2390 bs	2380 s	f
				2275 bs	2275 s	f
		1708 w	1708 w			g
1590 bs	1570 bs	1561 bs	1590 s	1560 bs	1536 bs	h
	1448 s		1526 s			h
1425 bs	1415 s	1427 bs	1453 s		1450 s	i
1344 m	1344 m	1348 m	1421 s	1430 bs	1422 s	j
			1350 m	1351 m	1350 m	k
1052 w	1051 w	1055 w		1165 w	1151 w	l
1027 m	1026 m	1026 m	1059 w	1055 w	1058 m	n
946 m	946 m	946 m	1032 m	1026 m	1028 s	n
			949 m	938 m	940 m	o
			880 m			p
		856 m	850 m			p
		803 m	820 m			q
		724 m	745 m			r
663 s	661 s	658 s	664 s	669 s	671 m	s
619 m	617 m	623 m	625 m	624 m	638 s	t
			605 m	602 vw	601 s	t
509 bm	510 bw	588 bm		529 bm	542 m	u
		541 bm	548 m		467 w	u
					455 vw	u
405 bm	400 bw	424 m	431 m	426 bm	434 w	u
					419 m	x
388 m	388 bw	386 vw	385 m	361 bm	413 vw	u
		379 w			377 s	v
		370 vw				u
		336 w	337 w	345 vw	371 vw	u
299 w	299 w	332 w	331 w	331 vw	344 vw	u
290 vw	291 vw	300 m	299 bw		337 m	u
285 w	285 w					v
273 w	274 w	275 m	277 m	292 bw	297 w	v
		271 w	274 m	270 m	292 vw	v
					280 w	v
					273 m	v

From reference to Table VI, Table VII, and Table VIII, it can be seen that nickel, cobalt, and magnesium tetrahydrate acetates exhibit absorptions in the cesium bromide region in the range  $300\text{--}550\text{ cm}^{-1}$  which are probably due to the librational modes of the bound water molecules.<sup>81</sup>

The infrared spectra of nickel, cobalt, and magnesium acetates in the 2 to 20 micron region are shown in Figure 9, Figure 10, and Figure 11, respectively. The dehydrated, hydrated, and deuterated compounds are compared at room temperature (solid lines) and at liquid nitrogen temperature (broken lines).

The cesium bromide spectra of nickel acetate dehyd., nickel acetate  $.4\text{H}_2\text{O}$ , and nickel acetate  $.4\text{D}_2\text{O}$  are presented in Figure 12. The far infrared spectra of cobalt and magnesium acetates, although not shown pictorially, are very similar to nickel acetate and are given in table form in Table VII and Table VIII, respectively.

b. Nickel acetate  $.2\text{DOH} .2\text{H}_2\text{O}$ . Since nickel acetate  $.4\text{H}_2\text{O}$  contains two water protons that are essentially free (Figure 3), and since these protons are not involved in hydrogen bonding, it would be assumed that they are held less tightly than the other water protons in the crystal structure. If this is the case, then they should be converted to deuterium atoms before the remaining hydrogen bonded protons are

Figure 9

Infrared Spectra of Nickel Acetate at  
Room Temperature and Liquid Nitrogen  
Temperature in the (4000-500  $\text{cm}^{-1}$ ) Region

\_\_\_\_\_ = Room Temperature

----- = Liquid Nitrogen Temperature

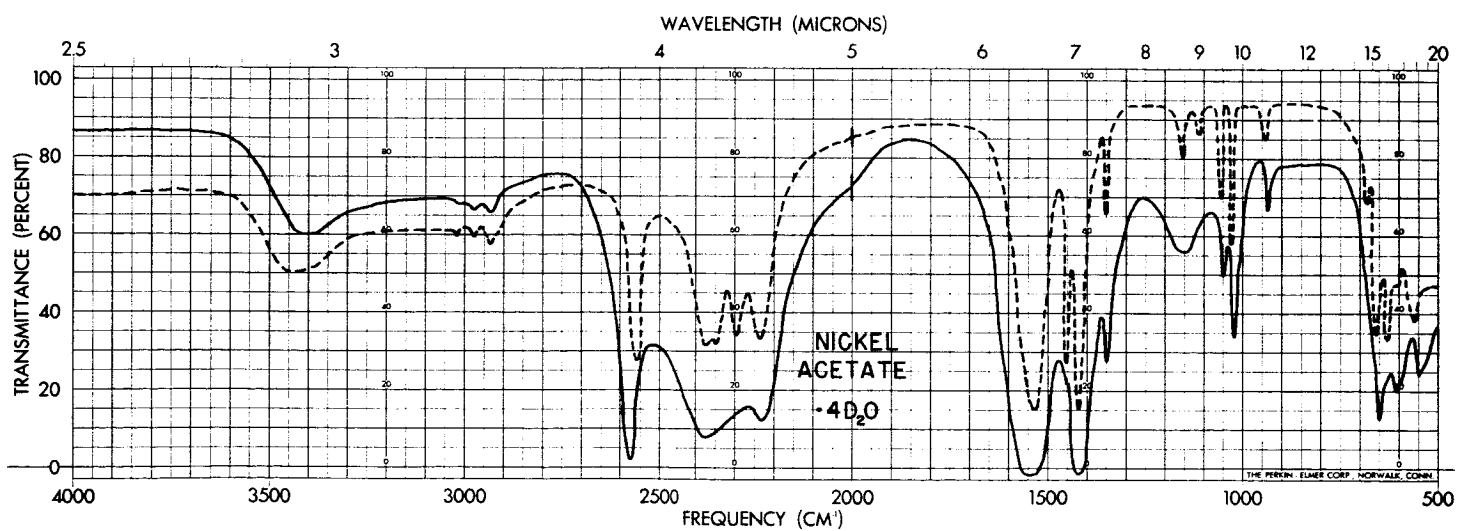
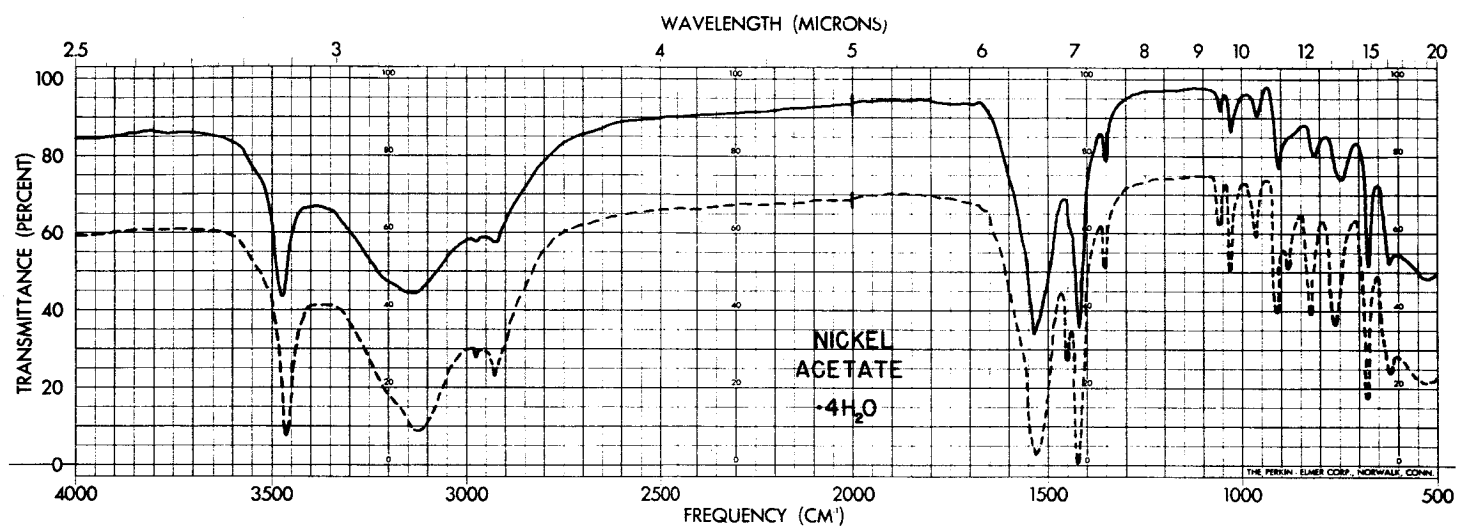
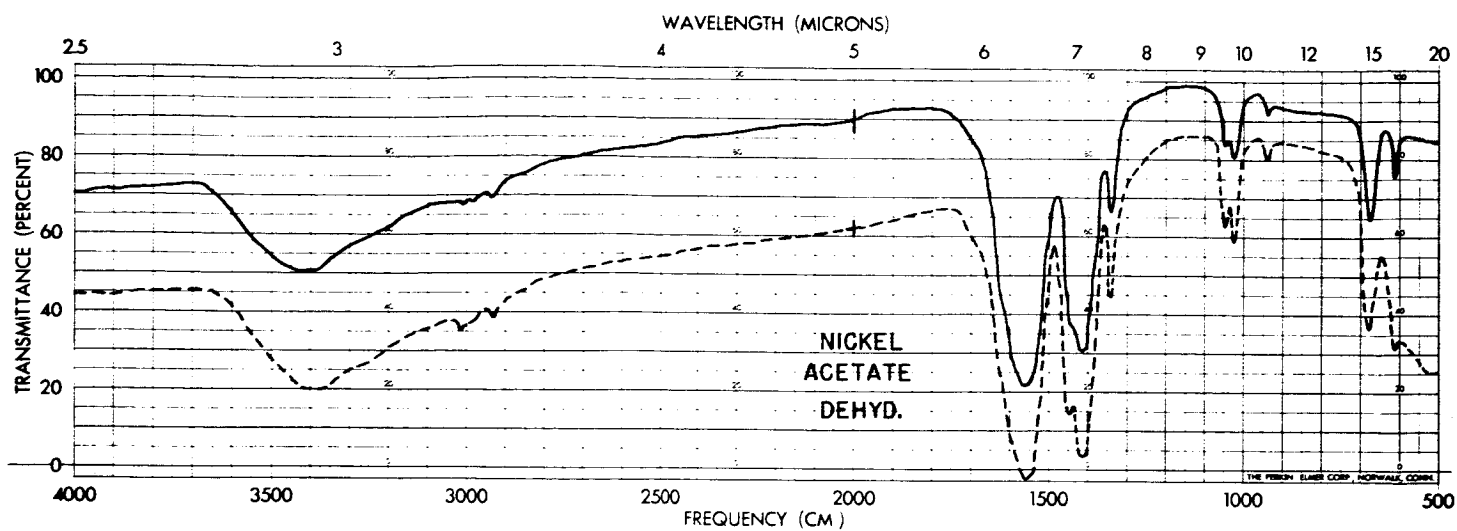


Figure 10  
Infrared Spectra of Cobalt Acetate at  
Room Temperature and Liquid Nitrogen  
Temperature in the ( $4000-500\text{ cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

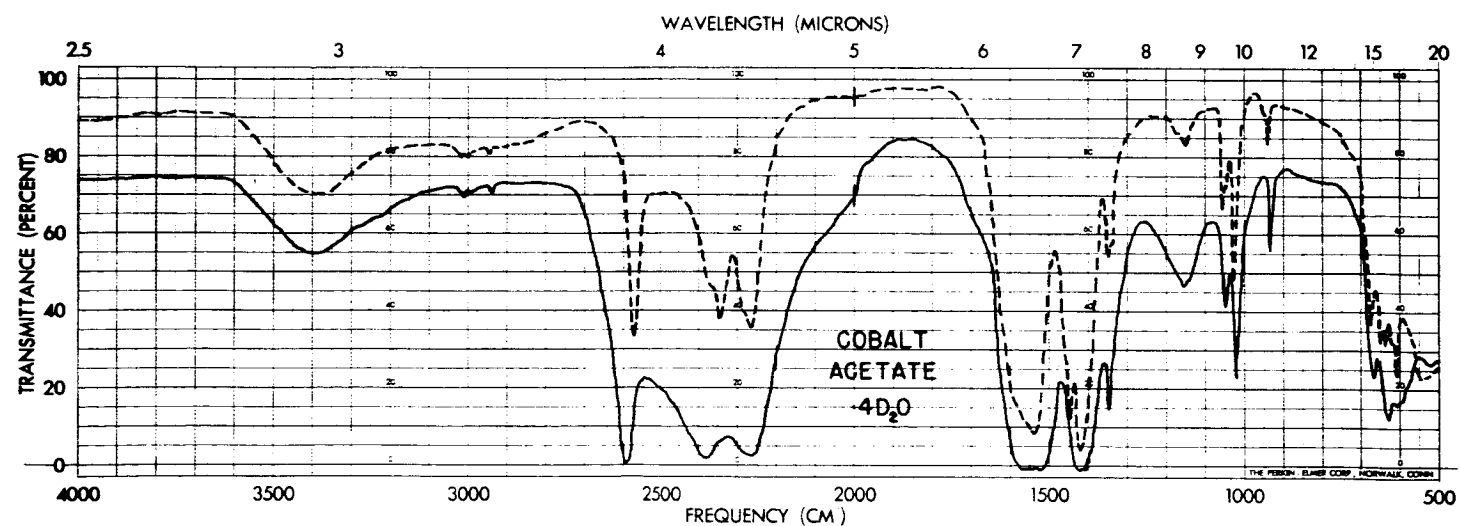
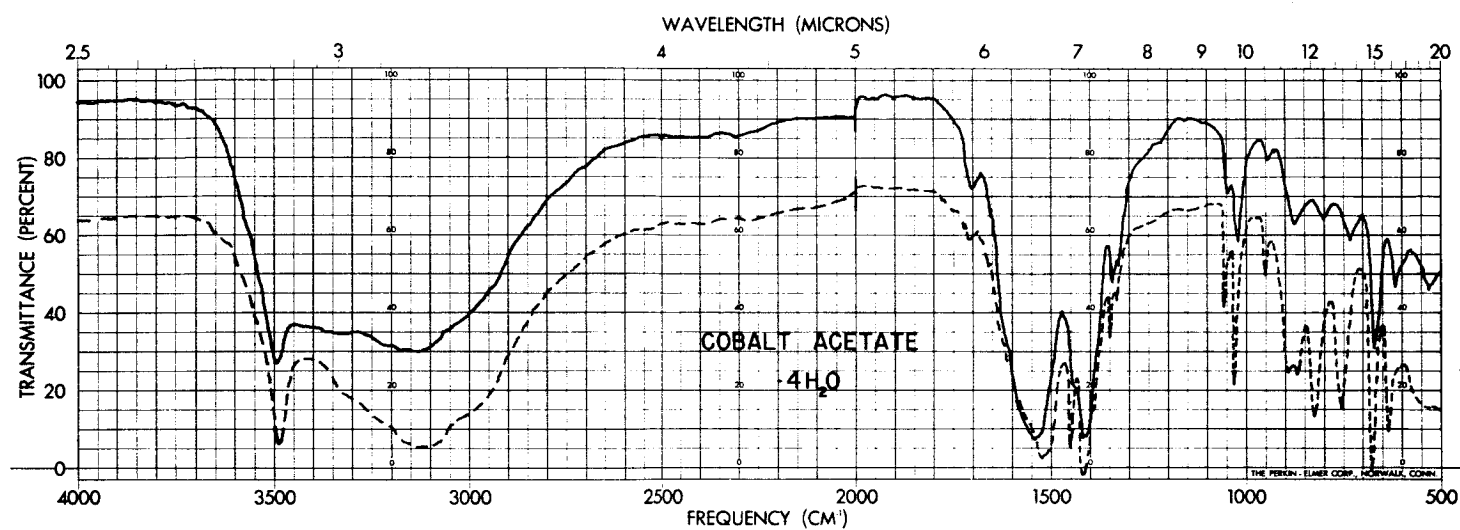
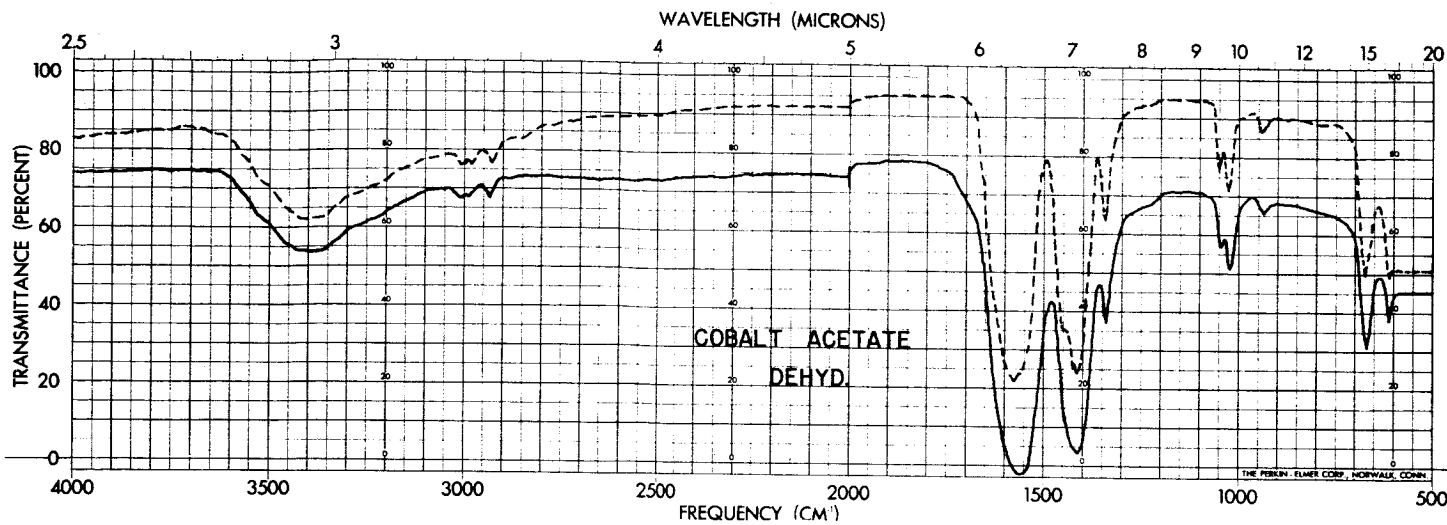


Figure 11  
Infrared Spectra of Magnesium Acetate at  
Room Temperature and Liquid Nitrogen  
Temperature in the (4000-500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

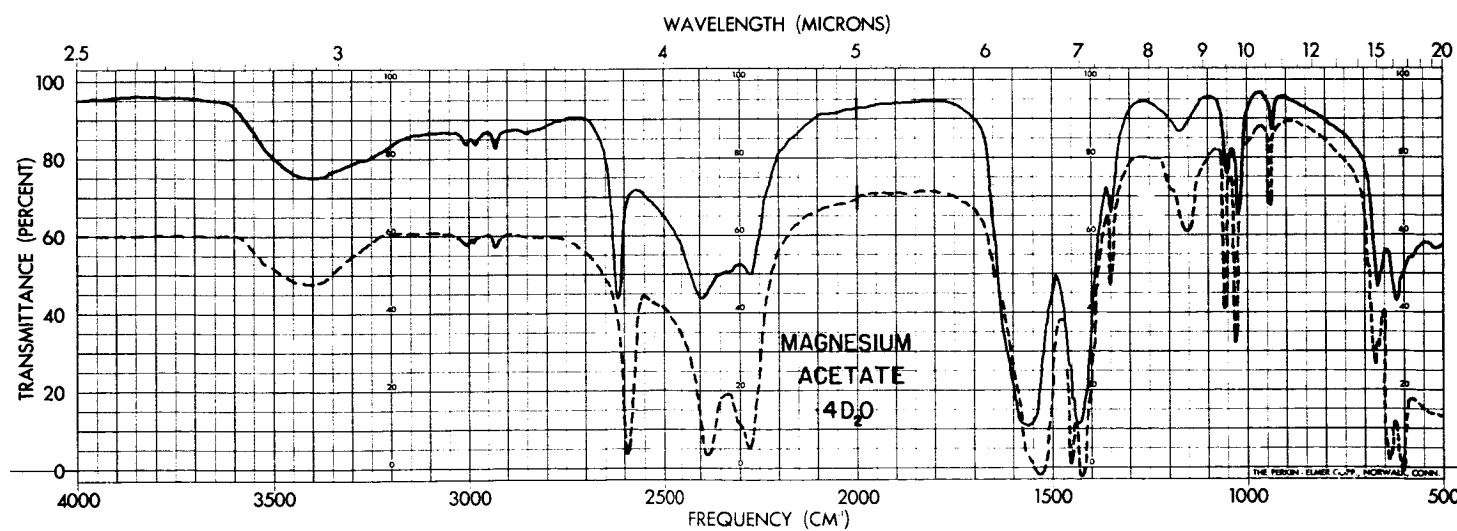
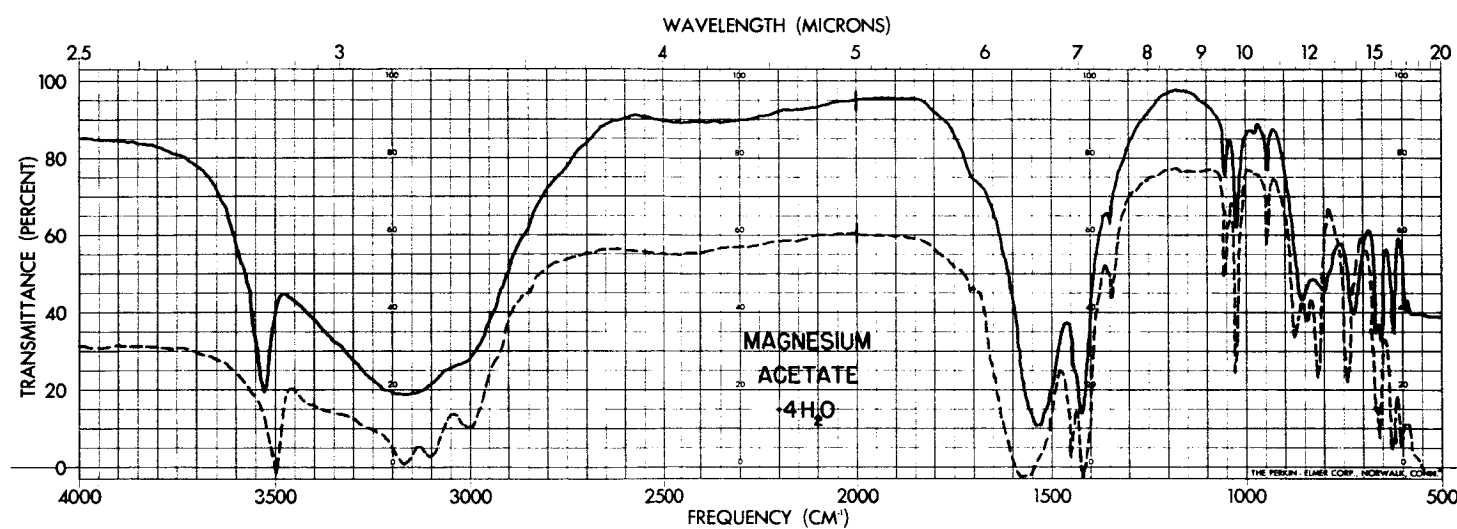
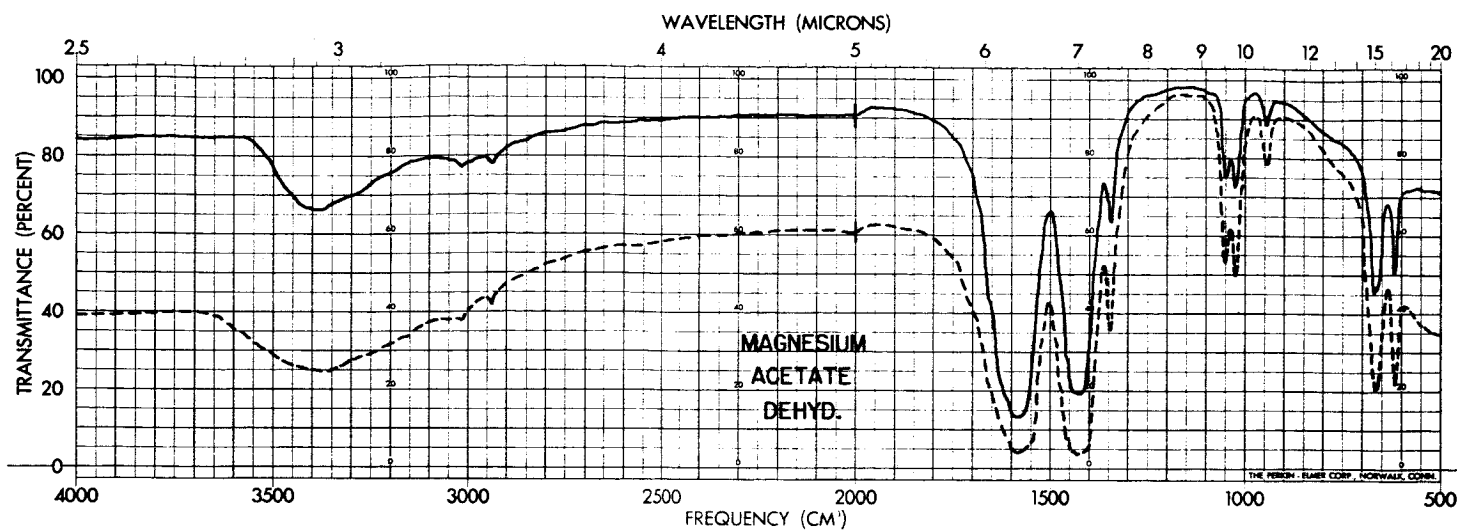
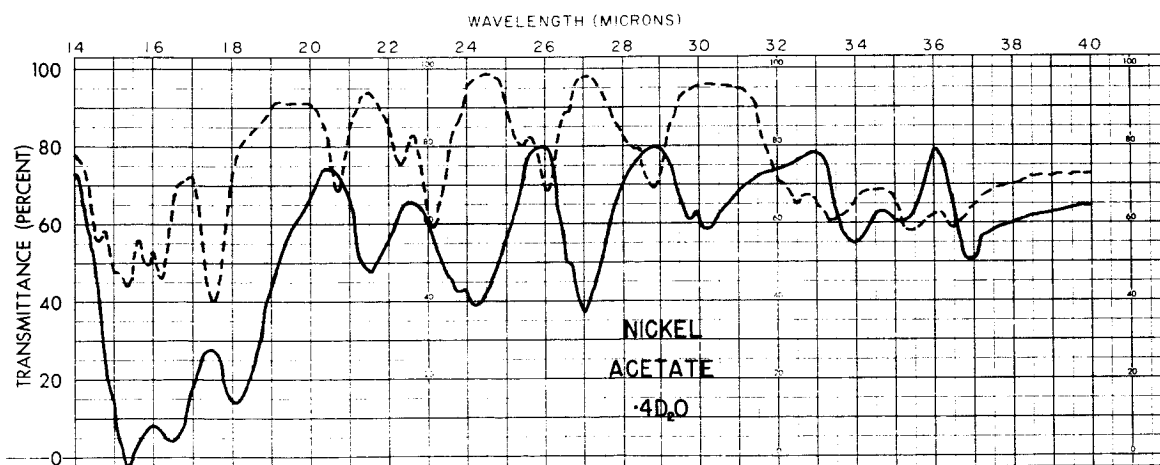
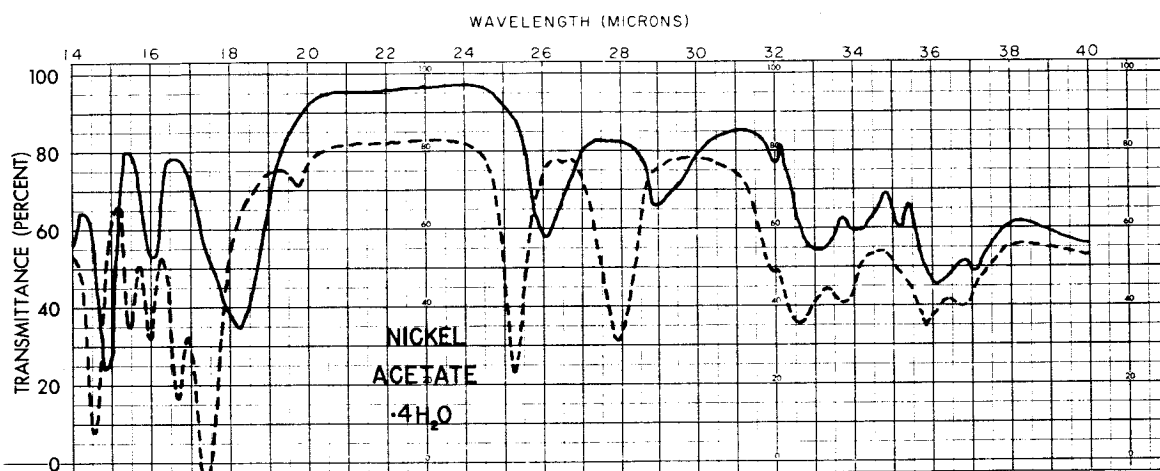
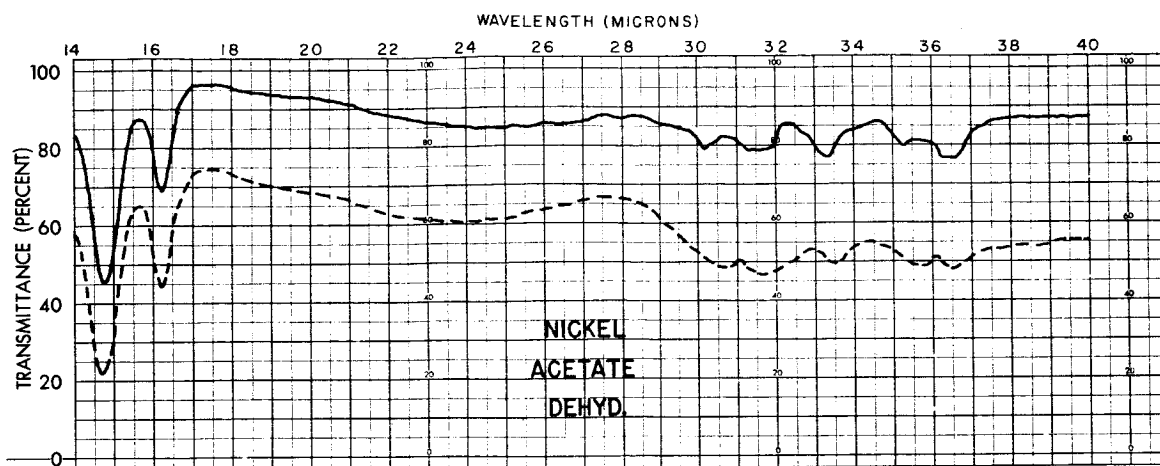




Figure 12  
Infrared Spectra of Nickel Acetate Dehyd.,  
.4H<sub>2</sub>O and .4D<sub>2</sub>O in the 14 to 40 Micron Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature



exchanged, in the deuteration process. Apparently this is the case as evidenced by Figure 13 which shows the infrared spectrum of nickel acetate  $\cdot 2\text{DOH} \cdot 2\text{H}_2\text{O}$  in the  $\text{D}_2\text{O}$  stretching region where only the free protons are exchanged for deuterium atoms, with the hydrogen bonded protons showing no evidence of exchange. This is another important factor in confirming the presence of these free water protons in the nickel acetate  $\cdot 4\text{H}_2\text{O}$  structure. It shows the ability to stop the exchange reaction after conversion of only the free protons giving a further insight into the nature of the bonding in this complex. The complete infrared spectrum of this deuterio-hydrate is presented in the 2 to 40 micron wavelength region in Figure 14.

c. Infrared spectra of nickel acetate  $\cdot 4\text{H}_2\text{O}$  using other sampling techniques. All infrared spectra shown pictorially or given in table form have been measured using the KBr pellet technique unless specifically stated otherwise. There have been numerous instances in the literature where workers have found erroneous results using the alkali halide pellet technique in the infrared studies of metal compounds. It has been found that in cases, exchange occurs between the metal of the matrix and the metal in the compound to be studied, when subjecting solids to the pressures required to form a satisfactory alkali halide pellet. In many cases di-metal compounds result. Great care was taken in this work to

Figure 13

Infrared Spectrum of Nickel Acetate  
.2DOH .2H<sub>2</sub>O in the (2100-2800 cm.<sup>-1</sup>) Region

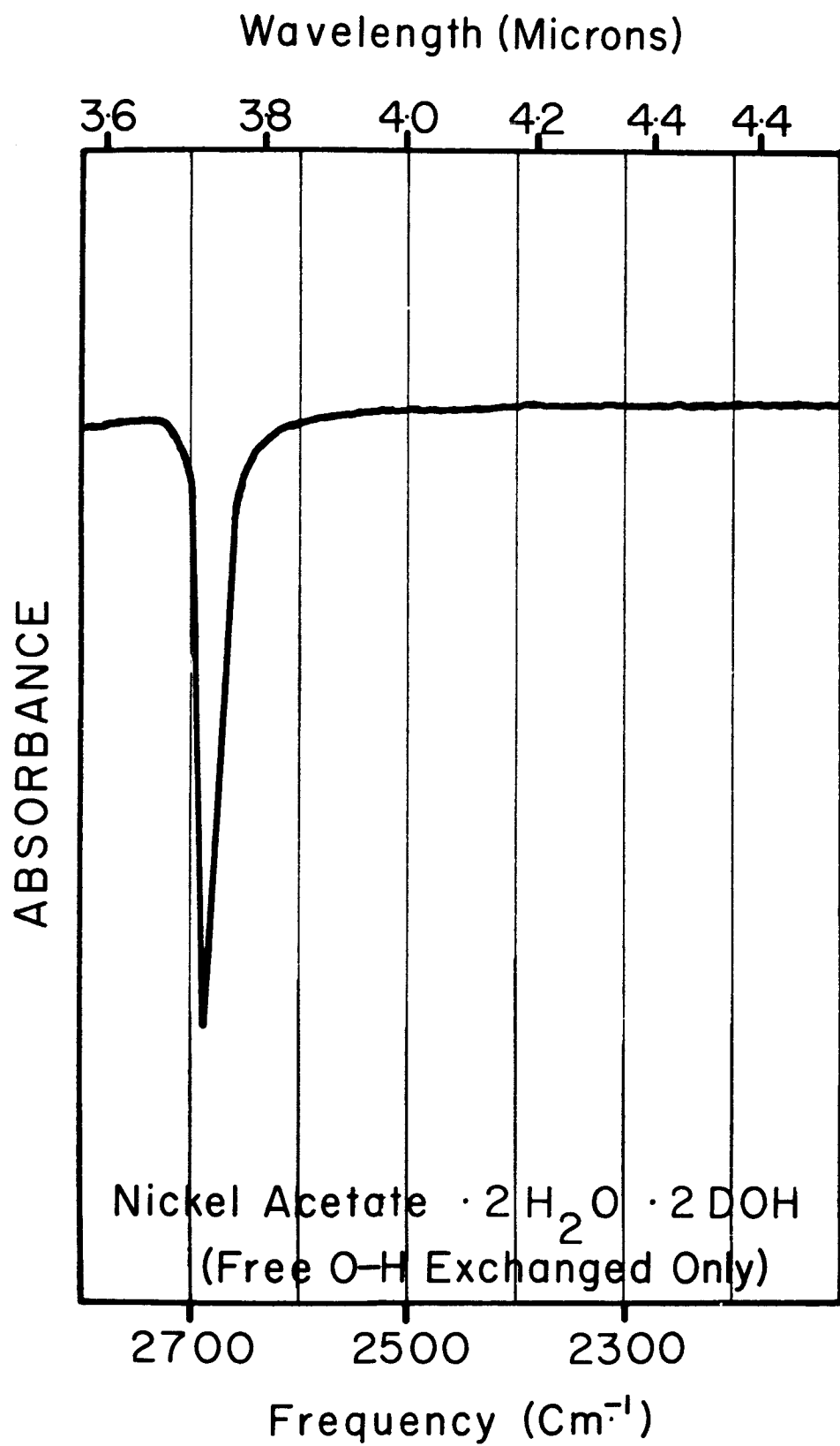
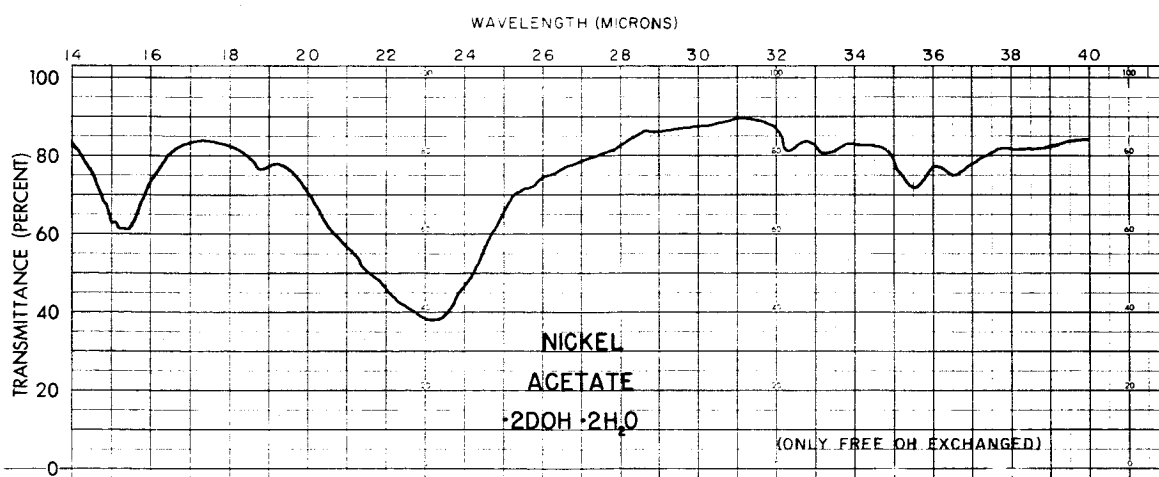
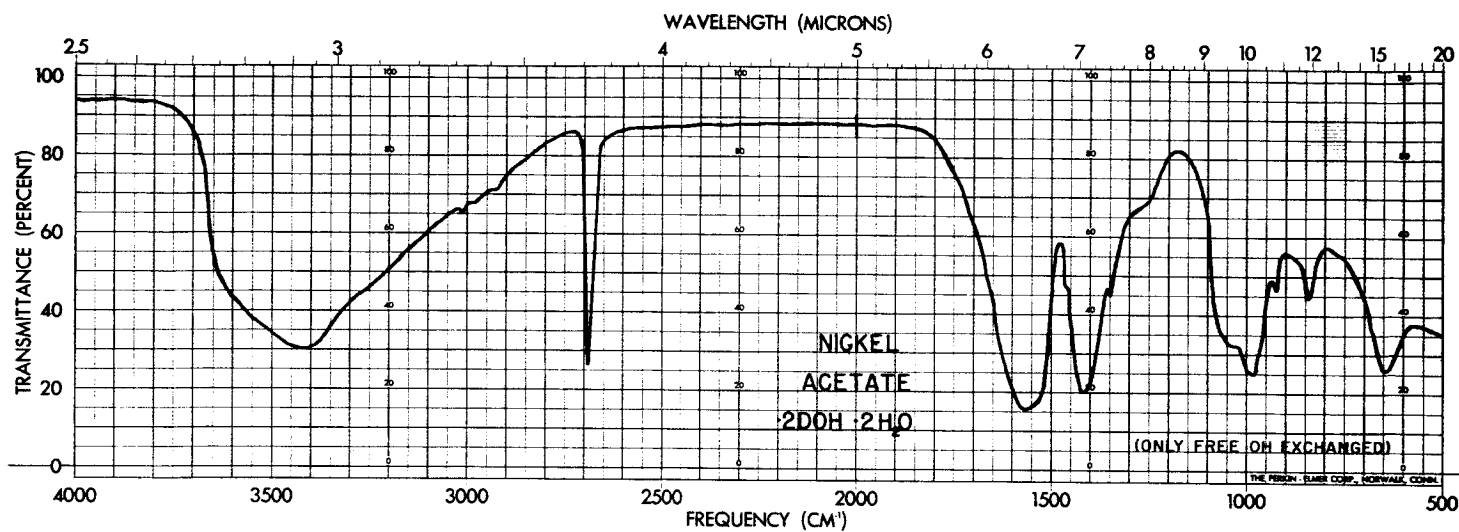


Figure 14

Infrared Spectrum of Nickel Acetate  
.2DOH .2H<sub>2</sub>O in the 2.5 to 40 Micron  
Region at Room Temperature



determine if any exchange was evident by examining the spectra of all the acetates by the following sampling methods:

(1) Nujol mull. The infrared spectrum of nickel acetate  $.4\text{H}_2\text{O}$ , obtained by hand grinding with mineral oil, is shown in Figure 15-A. The Nujol absorptions are labeled.

(2) Fluorolube mull. Since mineral oil obscures part of the previous spectra, the spectrum of nickel acetate  $.4\text{H}_2\text{O}$  is shown in Figure 15-B by mulling with Fluorolube. The Fluorolube absorptions are labeled.

(3) Deposited powder film. The infrared spectra of nickel acetate  $.4\text{H}_2\text{O}$  is shown in Figure 15-C as a powder film prepared by dissolving crystals of the salt in spectroscopic grade methanol and evaporating the solution to dryness on a rock salt window. Apparently the crystal structure of nickel acetate  $.4\text{H}_2\text{O}$  changes upon dissolving in methanol as can be seen by the disappearance of the free  $\text{H}_2\text{O}$  absorption using this method.

(4) Solution in  $\text{D}_2\text{O}$ . The infrared spectrum of nickel acetate  $.4\text{H}_2\text{O}$  is shown as an approximately 10% solution in 99.7%  $\text{D}_2\text{O}$  using an 0.015 mm. "Irtran" liquid cell in Figure 16-B. Obviously upon solution of this salt in  $\text{D}_2\text{O}$ , we are no longer observing the spectrum of the crystal, but the products formed upon dissolving. The free water protons are now all hydrogen bonded as would be expected. The three water



Figure 15  
Infrared Spectra of Nickel Acetate  $.4\text{H}_2\text{O}$  in  
the  $(4000-500\text{ cm}^{-1})$  Region Using Various  
Sampling Techniques  
A. = Nujol Mull  
B. = Fluorolube Mull  
C. = Deposited Powder Film

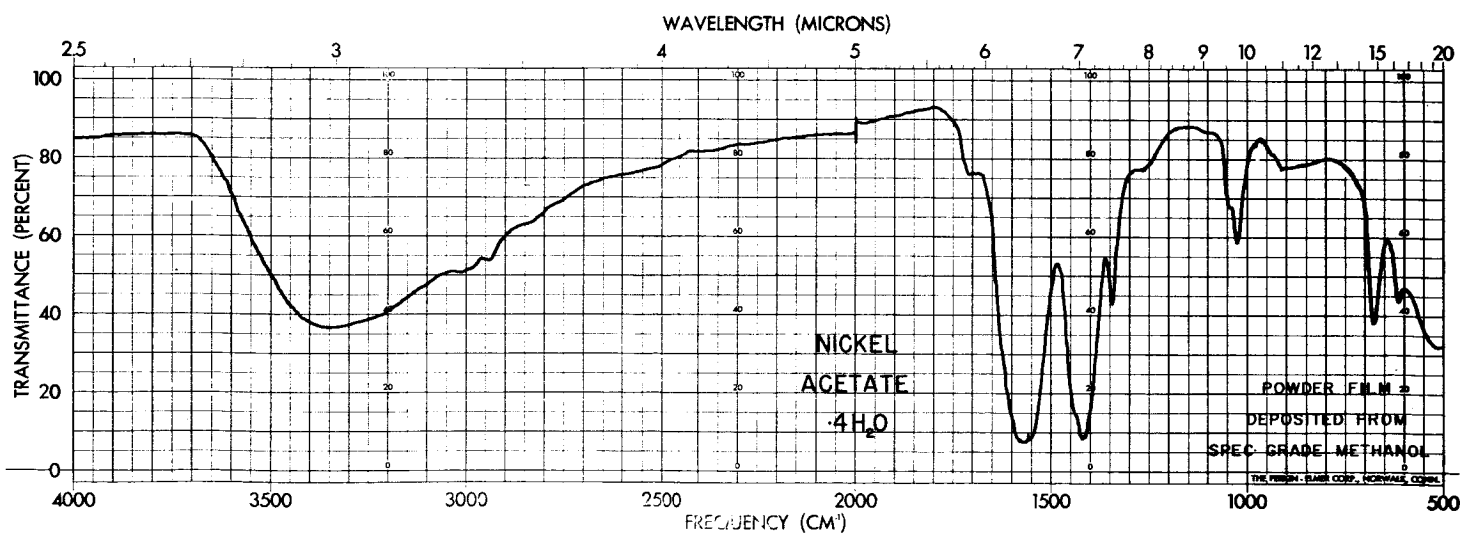
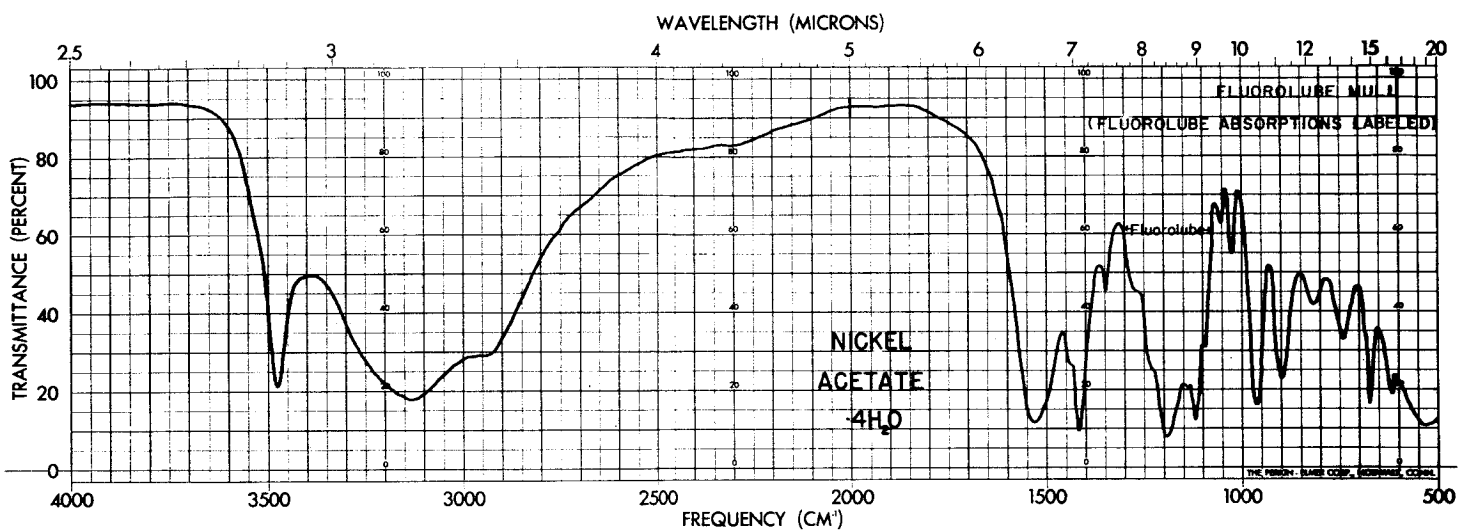
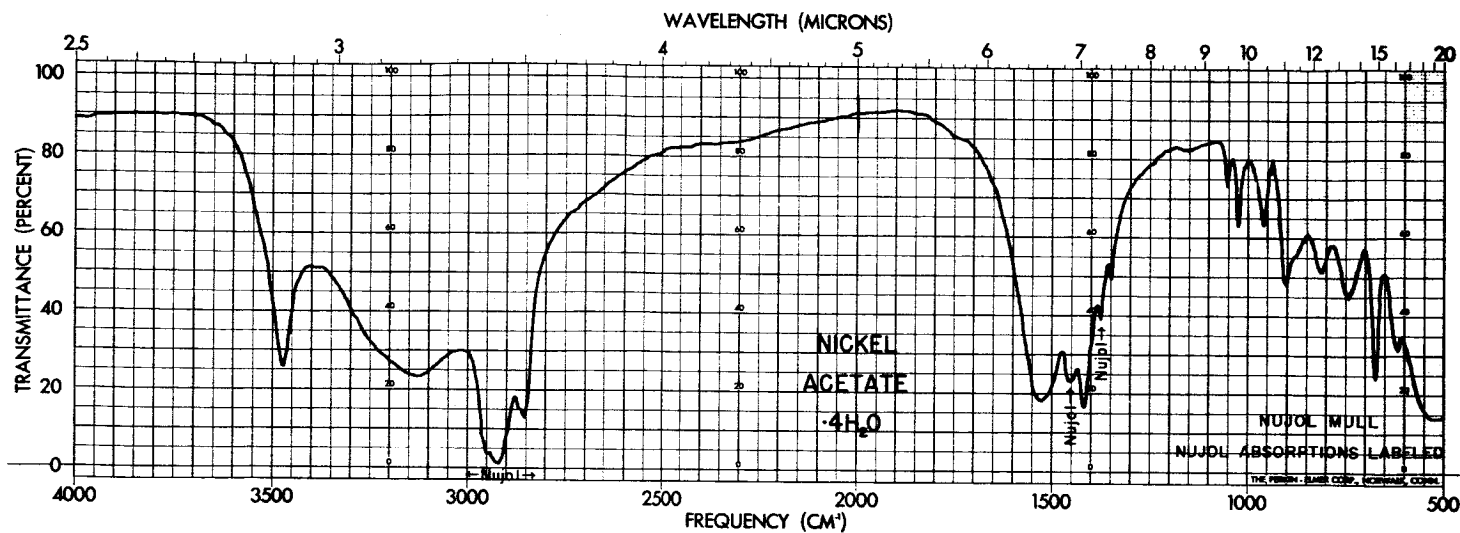
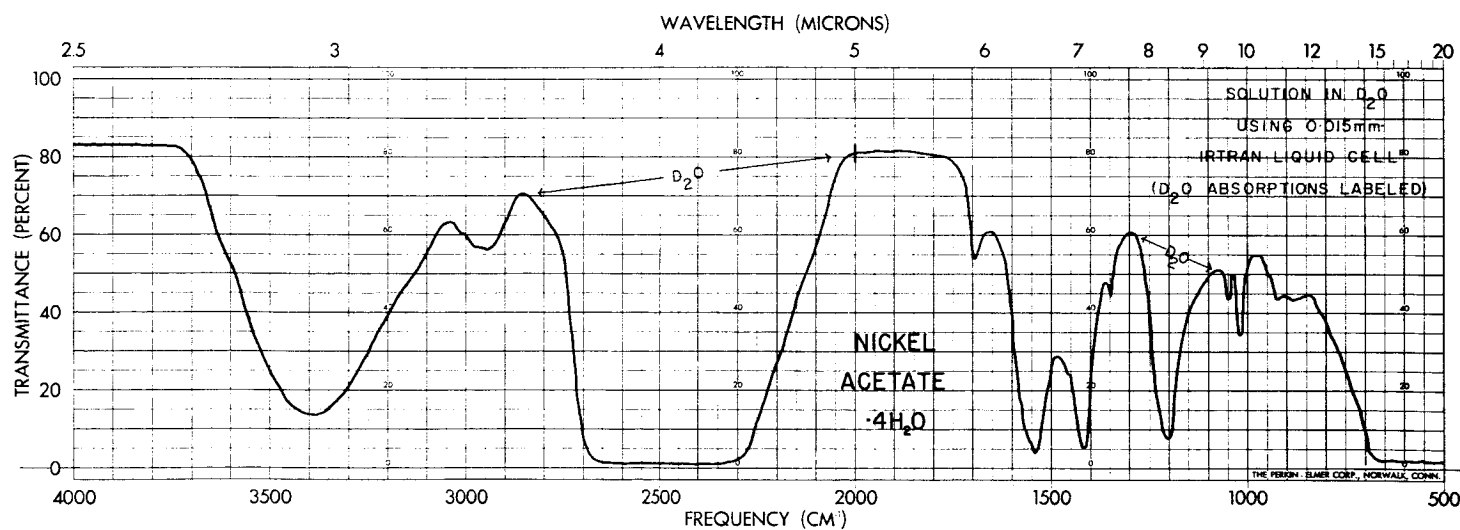
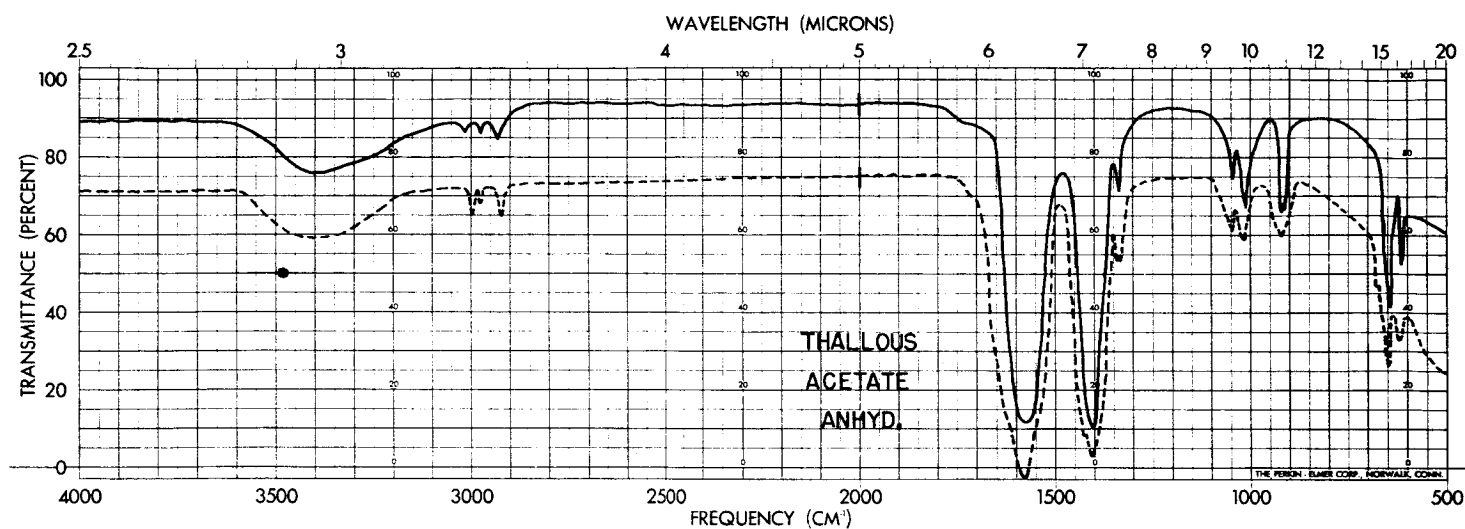


Figure 16

- A. Infrared Spectrum of Thallous Acetate Anhyd.  
(4000-500  $\text{cm}^{-1}$ )
- B. Infrared Spectrum of Nickel Acetate  $\cdot 4\text{H}_2\text{O}$  in  
the (4000-500  $\text{cm}^{-1}$ ) Region as a Solution in  
 $\text{D}_2\text{O}$  Using a 0.015 mm. Irtran Liquid Cell



vibrations in the  $724\text{--}904\text{ cm}^{-1}$  region have disappeared, showing that these absorptions are characteristic of the solid state spectra which is no longer present in solution. "Irtran" itself no longer transmits satisfactorily after about 14 microns.

The spectra of nickel acetate  $\cdot 4\text{H}_2\text{O}$  and all the other acetate complexes studied were sampled using all of the above techniques. It was found that in all cases the spectra in Nujol and Fluorolube agreed with the spectra of the acetates in KBr showing that in these complexes, no apparent interaction with the matrix occurs. The spectra shown herein are KBr pellet spectra unless labeled otherwise. It should be noted that KBr itself picks up water and the weak broad absorption at approximately  $3400\text{ cm}^{-1}$  appearing in the spectra of the dehydrated and deuterated acetates is due entirely to KBr water, since these compounds show no absorption in that region as Nujol or Fluorolube mulls, and since pure KBr pellets show a similar band.

(d) Manganese acetate. Manganese acetate  $\cdot 4\text{H}_2\text{O}$  exhibits a broad absorption at  $3275\text{--}3388\text{ cm}^{-1}$  which shifts to  $2340\text{--}2510\text{ cm}^{-1}$  in manganese acetate  $\cdot 4\text{D}_2\text{O}$  and disappears upon dehydration and is assigned as the  $\text{H}_2\text{O}$  stretching vibration of the coordinated water molecules. This hydrate also exhibits an absorption band at  $1706\text{ cm}^{-1}$  which shifts to  $1197\text{--}1220\text{ cm}^{-1}$  upon deuteration and disappears upon dehydration and is assigned as the  $\text{H}_2\text{O}$  bending vibration; while bands at  $882\text{ cm}^{-1}$ , and

760  $\text{cm}^{-1}$ , which shift upon deuteration and are removed upon dehydration can be analogously assigned to wagging, twisting, or rocking modes of the coordinated water as in nickel, cobalt, and magnesium tetrahydrate acetates. The cesium bromide absorption bands in the 300-550  $\text{cm}^{-1}$  region are also assigned to the librational modes of the coordinated water. The spectra of manganese acetate dehydrated,  $.4\text{H}_2\text{O}$ , and  $.4\text{D}_2\text{O}$  are shown at room temperature (solid lines) in Figure 17 and all absorption bands are tabulated and assigned in Table IX.

The infrared spectrum of manganese acetate  $.4\text{H}_2\text{O}$  is very useful since it indicates a structure very similar to that of cobalt, nickel, and magnesium tetrahydrate acetates, the major difference being that manganese acetate  $.4\text{H}_2\text{O}$  does not have any free water protons; i.e., all coordinated water protons are involved in hydrogen bonding. Since manganese acetate  $.4\text{H}_2\text{O}$  has no free water protons, and exhibits essentially only one coordinated water absorption (760  $\text{cm}^{-1}$ ) of moderate intensity at room temperature, then it can be assumed that this absorption is due to completely hydrogen bonded water molecules in manganese acetate  $.4\text{H}_2\text{O}$ , and that the two other water absorptions occurring in the 700-900  $\text{cm}^{-1}$  region in cobalt, nickel, and magnesium acetates  $.4\text{H}_2\text{O}$  are probably associated with the water molecules containing the free water protons.

Figure 17  
Infrared Spectra of Manganese Acetate at  
Room Temperature and Liquid Nitrogen  
Temperature in the (4000-500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

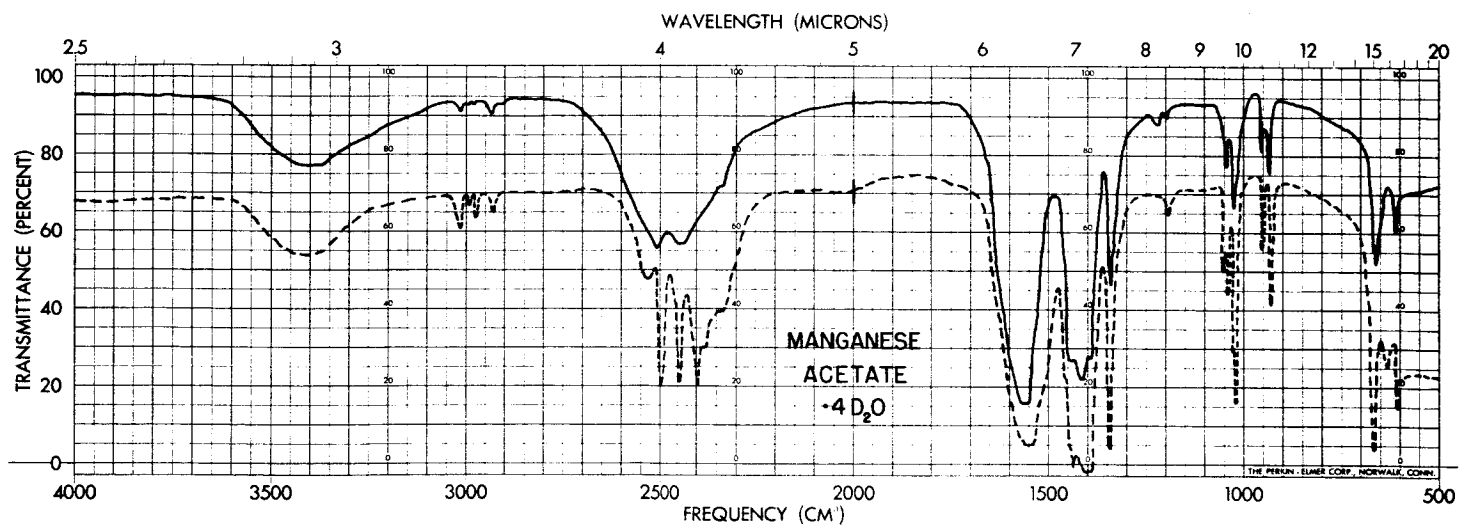
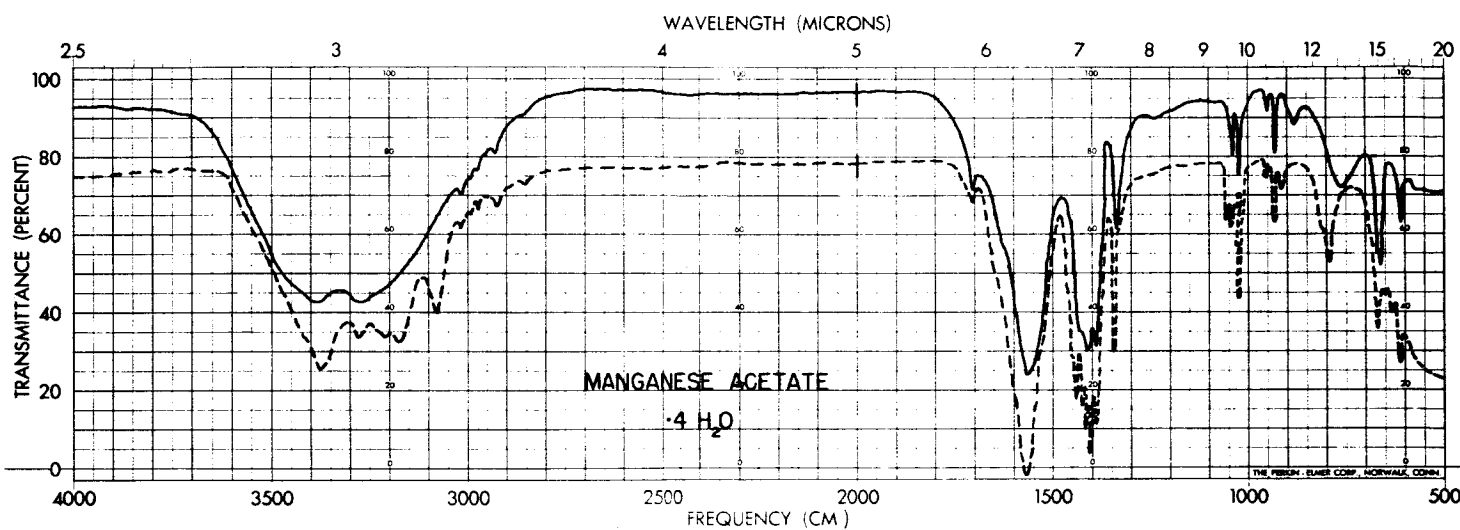
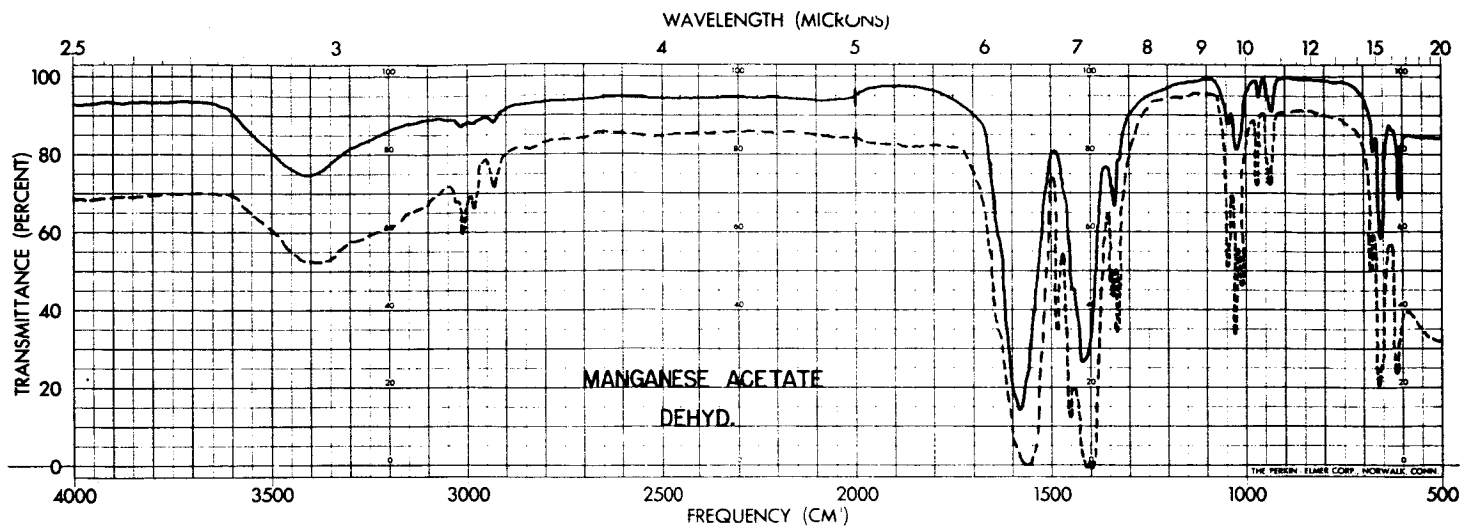




Table IX

Infrared Absorption Bands of Manganese Acetate Dehyd.,  $.4H_2O$  and  $.4D_2O$ 

Manganese Acetate Dehyd		Manganese Acetate. $.4H_2O$		Manganese Acetate. $.4D_2O$		Assn.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3388 bs 3275 bs	3376 s 3280 s 3212 s 3172 s 3080 s			a b b b b c
3016 vw	3026 vw 3010 vw	3015 vw 2992 vw	3015 vw 2992 vw	3015 vw 2994 vw	3015 vw 2993 vw	c c
2985 vw	2983 vw	2972 vw	2972 vw	2973 vw	2973 vw	c
2936 vw	2930 w	2927 vw	2927 vw	2935 vw 2510 s	2930 vw 2530 w	d f
				2440 bs	2497 s 2444 s	f f
					2396 s 2380 sh	f f
				2340 vw	2350 w	f
1580 bs	1560 bs	1705 m 1570 bs	1705 m 1568 bs	1560 bs	1558 bs	g h
1442 s	1482 m 1452 s	1432 s	1439 s	1440 sh	1439 s	y i
1425 s		1415 s	1425 s 1418 s	1416 s		i j
	1408 s		1408 s			j
	1398 s	1392 s	1396 s	1396 sh	1400 bs	j
1342 w	1347 w	1342 m	1342 m	1344 m	1344 m	k k
1337 w	1341 w					m
1324 w	1334 w			1220 w 1197 w	1194 vw	m m
			1052 w		1052 w	n
1045 w	1047 w	1044 w	1046 w	1044 w	1046 w	n
			1043 w		1043 w	n
			1033 m		1031 m	n
1025 m	1027 m	1025 m	1024 m	1025 m	1024 m	n n
	1018 w					n
966 w	971 w	951 w	954 w	952 w	954 w	6
929 m	937 w	932 m	933 m	932 m	933 m	o
			913 m			p
		882 w 760 m	792 s			p q

Table IX (continued)

Infrared Absorption Bands of Manganese Acetate Dehyd., .4H<sub>2</sub>O and .4D<sub>2</sub>O

Manganese Acetate Dehyd		Manganese Acetate.4H <sub>2</sub> O		Manganese Acetate.4D <sub>2</sub> O		Assn.
Room Temp Cm. <sup>-1</sup> I	Liq.N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq.N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq.N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
677 vw	680 m	670 vw	668 s	670 w	668 s	s
	661 s	664 s		664 s		s
653 s	651 s		648 m			s
			635 s		634 w	t
612 s	610 m	612 s	612 s	612 s	613 m	t
			590 m			u
			543 m	529 w		u
	514 vw					x
494 m	496 m	487 m	489 vw	482 m	481 m	x
			481 m	436 bm	448 bm	x
				407 bm		u
		342 vw	354 m	360 bm	345 bw	u
337 vw		337 vw		341 bw		v
330 vw	329 vw	330 vw	325 w	330 w		v
317 m	317 m	317 vw				v
314 m	314 m	310 vw	313 w			v
			305 w	303 w		u
299 m	298 m	298 m	299 m	298 m	299 m	v
283 m	283 m	283 w	282 w	283 w	282 w	v
274 m	273 m	274 m	275 m	273 w	274 w	v
		264 vw				u

3. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Liquid Nitrogen Temperature (4000-250 cm.<sup>-1</sup>)

a. Nickel, cobalt, and magnesium acetates. The infrared spectra from 2 to 20 microns of nickel, cobalt, and magnesium acetates at liquid nitrogen temperature are shown in Figure 9, Figure 10, and Figure 11 (dotted lines), respectively. The free H<sub>2</sub>O stretching absorptions sharpen, intensify, and shift slightly to lower frequencies upon cooling to liquid nitrogen temperature. This effect is similarly exhibited by the deuterated hydrates.

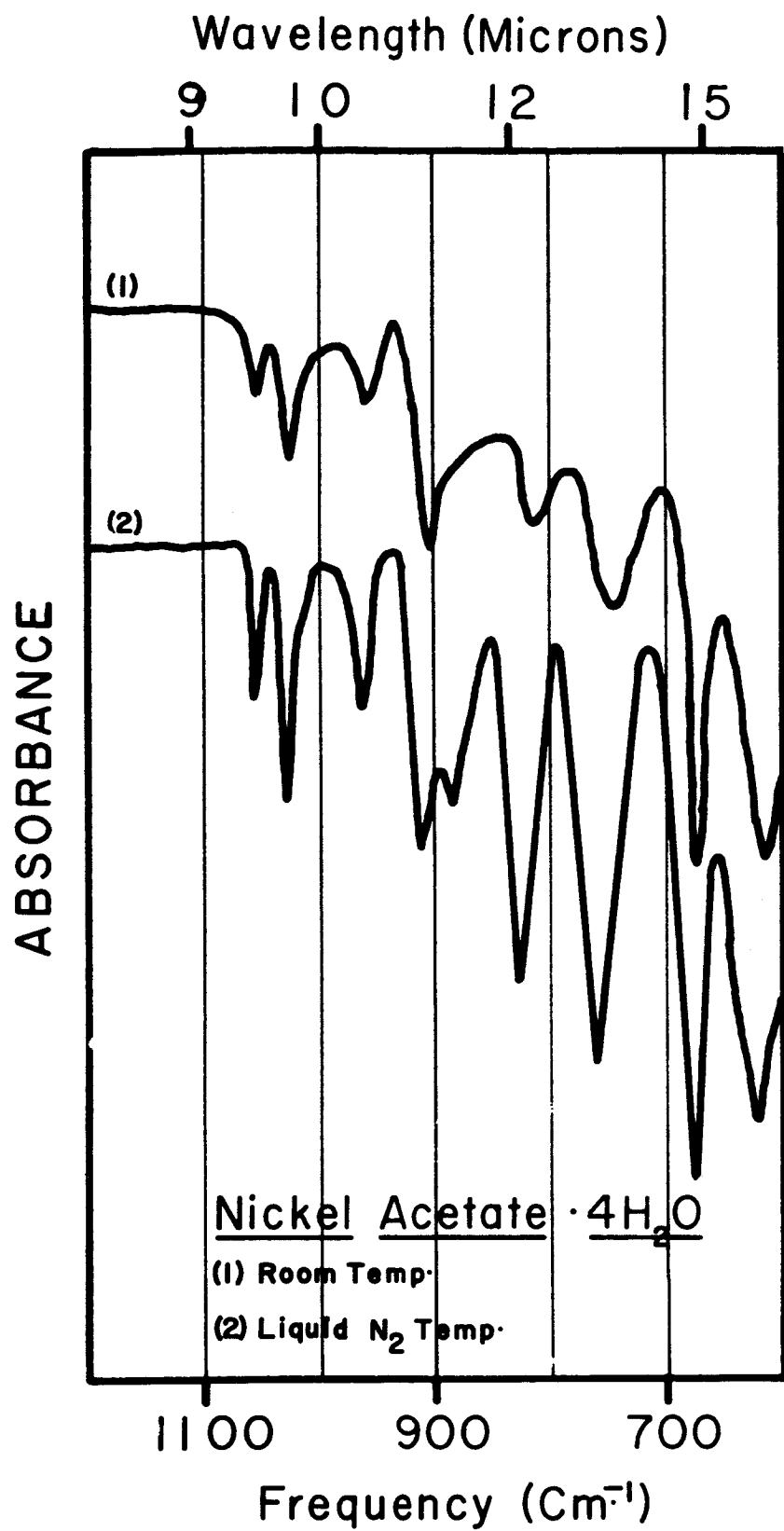
The broad hydrogen bonded H<sub>2</sub>O stretching absorption is seen to exhibit splitting at liquid nitrogen temperature in the normal hydrates, and this effect is readily apparent at low temperature in the deuterated hydrates. This effect is probably due to the different types of bound hydrogen bonded water molecules in the crystal lattice. Since the hydrogen bond lengths are slightly different for certain coordinated water protons, and since there are intra- and inter- molecular hydrogen bonds, it would be expected that under high resolution and lowered temperature that these factors would be evidenced by the splitting of the broad hydrogen bonded water absorption in the stretching region.

The coordinated water absorption bands in the 700-

910  $\text{cm}^{-1}$  region also sharpen and intensify on cooling to liquid nitrogen temperature as shown in Figure 18, which compares the spectrum of nickel acetate  $\cdot 4\text{H}_2\text{O}$  at room temperature and at liquid nitrogen temperature in this region. The higher frequency band of the three is seen to split into a doublet when the temperature is lowered to approximately 85°K. The spectra of nickel acetate dehyd.,  $\cdot 4\text{H}_2\text{O}$  and  $\cdot 4\text{D}_2\text{O}$  are shown at liquid nitrogen temperature in the cesium bromide region in Figure 12 (broken lines). As can be seen, the librational modes of the coordinated water molecules are apparently extremely temperature sensitive. Table VI, Table VII, and Table VIII give the complete absorption bands and assignments for nickel, cobalt, and magnesium acetates, respectively, at liquid nitrogen temperature in the sodium chloride and cesium bromide regions.

b. Manganese acetate. The infrared spectra of manganese acetate dehyd.,  $\cdot 4\text{H}_2\text{O}$  and  $\cdot 4\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) in Figure 17. Other than the free  $\text{H}_2\text{O}$  stretching absorption, which is absent from the spectrum of manganese acetate  $\cdot 4\text{H}_2\text{O}$ , this hydrate exhibits a similar infrared spectrum to nickel, cobalt, and magnesium tetrahydrate acetates. The complete infrared spectra of manganese acetate dehyd.,  $\cdot 4\text{H}_2\text{O}$  and  $\cdot 4\text{D}_2\text{O}$  are tabulated in Table IX and absorption band assignments are given. The discussion given in the preceding section is applicable to manganese

Figure 18  
Infrared Spectrum of Nickel Acetate  $4H_2O$  at  
Room Temperature and Liquid Nitrogen  
Temperature in the Region  $(600-1200\text{ cm}^{-1})$



acetate except for the free  $\text{H}_2\text{O}$  absorptions. It is interesting to note that the hydrogen bonded water stretching region of the  $.4\text{H}_2\text{O}$  species and especially the  $.4\text{D}_2\text{O}$  compound, at liquid nitrogen temperature, show more splittings than the nickel, cobalt, and magnesium hydrates as would be expected since all four coordinated water molecules are hydrogen bonded in manganese acetate  $.4\text{H}_2\text{O}$ . Unfortunately, X-ray diffraction data is not available for manganese acetate  $.4\text{H}_2\text{O}$ . Probably intra- and inter-molecular hydrogen bonds are also present in the structure of manganese acetate  $.4\text{H}_2\text{O}$  thus further complicating exact band splitting assignments in the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching regions.

#### 4. Acetate Vibrations.

No mention has been made of vibrations of the acetate group in the previous discussions. Since vibrations of this group have been studied by other workers who have given assignments for these vibrations in sodium acetate, no detailed account of these frequencies will be given unless new or interesting results have been found as a result of this research. Acetate band assignments and frequencies of these vibrations are given in table form herein, since essentially only these absorptions have been reported previously for anhydrous sodium acetate. Acetate vibrations have been assigned by analogy with the assignments given for sodium acetate.<sup>9,12,35,37,86</sup>

Tables VI, VII, VIII and IX give acetate assignments

for nickel, cobalt, magnesium, and manganese acetates, respectively. Vibrations of the acetate group in these complexes can generally be characterized by absorptions at 2928-3015  $\text{cm}^{-1}$  ( $\text{CH}_3$  stretching--symmetric and asymmetric), 1532-1590  $\text{cm}^{-1}$  (asymmetric  $\text{CO}_2$  stretching), 1324-1453  $\text{cm}^{-1}$  (symmetric  $\text{CO}_2$  stretching and asymmetric and symmetric  $\text{CH}_3$  bending), 1011-1059  $\text{cm}^{-1}$  ( $\text{CH}_3$  rocking), 929-971  $\text{cm}^{-1}$  (C-C stretching), 631-695  $\text{cm}^{-1}$  ( $\text{CO}_2$  symmetric bending), 601-638  $\text{cm}^{-1}$  ( $\text{CO}_2$  rocking), and at approximately 450  $\text{cm}^{-1}$  ( $\text{CO}_2$  rocking).

It is interesting to note that the broad, strong absorption at approximately 1300-1500  $\text{cm}^{-1}$  at room temperature in these complexes generally shows only two well defined absorptions, the symmetric  $\text{CO}_2$  stretching and  $\text{CH}_3$  bending absorptions. There should, however, be more absorptions in this region since the asymmetric  $\text{CH}_3$  bending vibrations should occur in this energy region. Upon cooling to liquid nitrogen temperature, however, this broad band usually splits into four sharp peaks, characteristic of the  $\text{CO}_2$  symmetrical stretching and the  $\text{CH}_3$  asymmetrical and symmetrical bending vibrations.

It was observed that in cases many acetate fundamentals were observed to split into doublets or triplets at liquid nitrogen temperature in the KBr pellet spectra. There was a possibility that this was caused by interactions with the matrix material so all the acetates were observed at liquid



nitrogen temperature as mulls and as deposited powder films on rock salt windows to determine if this phenomena was caused by the KBr. The same splittings were readily apparent at liquid nitrogen temperature in the mull and powder film spectra, showing that this effect is apparently inherent in the acetate complexes which show it. Reliable and accurate results were again obtained using KBr thus indicating possible interactions between vibrations which give rise to these splittings at liquid nitrogen temperature.

The infrared studies of the acetate group made by other investigators did not extend below about  $350\text{ cm}^{-1}$  so that absorptions found in this region are new. Nickel, cobalt, magnesium, and manganese acetates give rise to generally four somewhat weak, broad absorptions between  $250$  and  $350\text{ cm}^{-1}$ . Since these absorptions are present in the dehydrated, hydrated, and deuterated forms, they cannot be coordinated water absorptions. Blank KBr pellet spectra do not show these absorptions. It is interesting to note that these low energy absorptions do not increase in intensity or sharpen at liquid nitrogen temperature; if anything, they remain the same as at room temperature or in cases appear to be less well defined. The only assignment that can be made at this time, and it is a tentative one, for these hitherto unreported absorptions, is that they are possibly due to librational modes of the whole molecule within

the crystal structure as differentiated from the librational motions of the coordinated water molecules within the molecular unit.

#### 5. Infrared vs. X-ray Data.

The infrared data tend to substantiate the structures of nickel, cobalt, and magnesium tetrahydrate acetates as established by X-ray methods. The infrared results alone would indicate that nickel, cobalt, and magnesium acetates have a similar structure. Although the structure of manganese acetate  $.4H_2O$  has not been reported, it would appear from the infrared analysis that it has a structure similar to the other three hydrates, except for the free water protons, which it does not have. Hence all water protons in manganese acetate  $.4H_2O$  are involved in either intra- or inter- molecular hydrogen bonding. Other than this, it is suggested that manganese acetate  $.4H_2O$  has a structure somewhat similar to nickel, cobalt, and magnesium tetrahydrate acetates.

van Neikerk and Schoening state that the metal-water and metal-oxygen bonds in nickel and cobalt acetates  $.4H_2O$  are "probably essentially ionic". Assumedly this statement is solely based on their bond distance measurements. Bond distance measurements alone, however, cannot always give a truly precise indication of the nature of the bonding in metallic complexes, such as the metallic acetate complexes.

Since the infrared analysis presented does not indicate absorptions assignable to a metal-oxygen (acetate) bond, it appears from infrared and X-ray data as though these bonds are probably ionic. However, according to Nakamoto and co-workers, the wagging, twisting, or rocking modes characteristic of coordinated water molecules will not be present in the infrared spectra unless there is covalent character attached to the metal-water bonds. Since these absorptions are present in the four tetrahydrate acetates studied, there probably is some covalent character attached to the metal-water bonds in these complexes.

## B. Trihydrate Acetates

### 1. Infrared Spectra of Normal Hydrates, Deuterated Hydrates and Anhydrous Analogs at Room Temperature (4000-250 $\text{cm}^{-1}$ )

a. Lead acetate. Lead acetate  $\cdot 3\text{H}_2\text{O}$  is characterized by a broad moderate absorption at approximately  $3400 \text{ cm}^{-1}$  which shifts to  $2550 \text{ cm}^{-1}$  with retention of its form upon preparation of lead acetate  $\cdot 3\text{D}_2\text{O}$ , and which is absent in the spectrum of dehydrated lead acetate. This absorption is assigned as the  $\text{H}_2\text{O}$  stretching vibration of the hydrogen bonded water molecules. This trihydrate has an absorption at  $1660 \text{ cm}^{-1}$  which shifts to  $1210 \text{ cm}^{-1}$  in the deuterated hydrate and is absent in the spectrum of the dehydrated species and is assigned as the  $\text{H}_2\text{O}$  bending vibration of the coordinated water. No water

absorptions were evident in the  $700\text{--}900\text{ cm}^{-1}$  region and no librational modes of coordinated water molecules were present in the cesium bromide region. The infrared spectra of lead acetate dehydrated,  $.3\text{H}_2\text{O}$ , and  $.3\text{D}_2\text{O}$  are shown in the  $4000\text{--}500\text{ cm}^{-1}$  region in Figure 19 and the complete spectra from 2.5 to 40 microns are tabulated with band assignments in Table X.

b. Sodium acetate. Sodium acetate  $.3\text{H}_2\text{O}$  has a broad strong absorption at  $3175\text{--}3430\text{ cm}^{-1}$  at room temperature which shifts to  $2384\text{--}2590\text{ cm}^{-1}$  in the spectrum of sodium acetate  $.3\text{D}_2\text{O}$  and which is absent from the spectrum of anhydrous sodium acetate and can be assigned as the  $\text{H}_2\text{O}$  stretching vibration of the coordinated water. It is interesting to note that this absorption possesses some structure at room temperature as can be seen from Figure 20, which shows the infrared spectra of sodium acetate anhydrous  $.3\text{H}_2\text{O}$  and  $.3\text{D}_2\text{O}$  in the  $4000\text{--}500\text{ cm}^{-1}$  region. This trihydrate acetate also has an absorption at  $1635\text{--}1695\text{ cm}^{-1}$  at room temperature which shifts to  $1196\text{--}1233\text{ cm}^{-1}$  in sodium acetate  $.3\text{D}_2\text{O}$  and which is absent from the spectrum of anhydrous sodium acetate. This absorption is assigned as the  $\text{H}_2\text{O}$  bending vibration of the coordinated water. Sodium acetate  $.3\text{H}_2\text{O}$  has an absorption at  $795\text{ cm}^{-1}$  at room temperature which shifts in the deuterated hydrate and which is absent in the spectrum of anhydrous sodium acetate and is assigned as a wagging, twisting, or rocking vibration of the

Figure 19  
Infrared Spectra of Lead Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000-500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

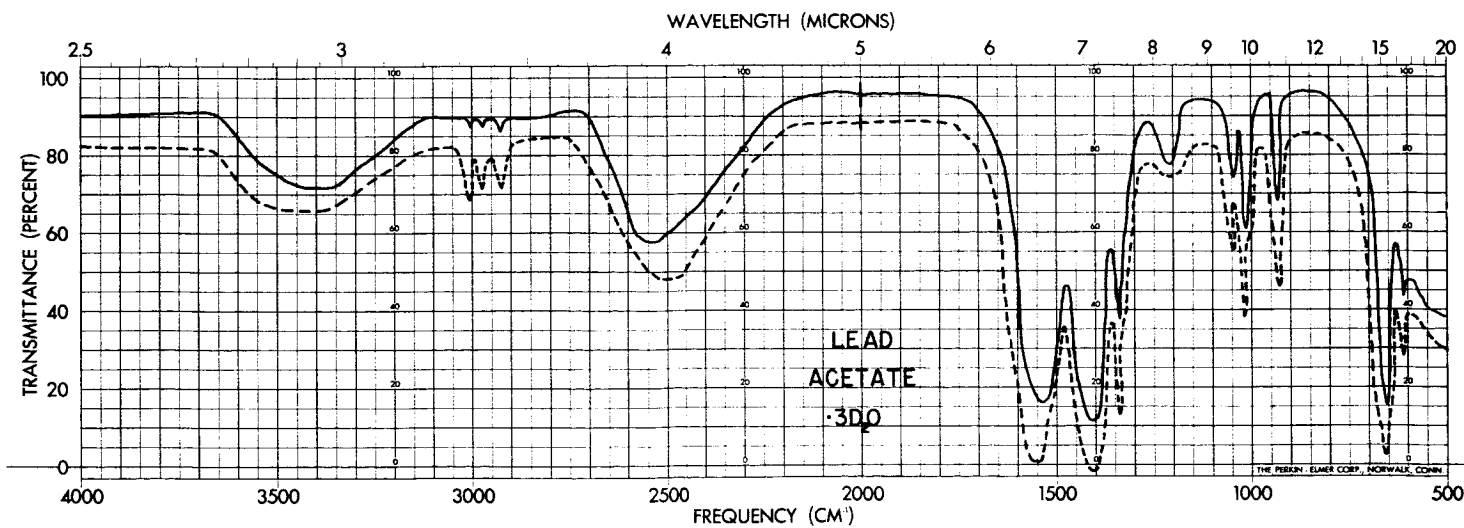
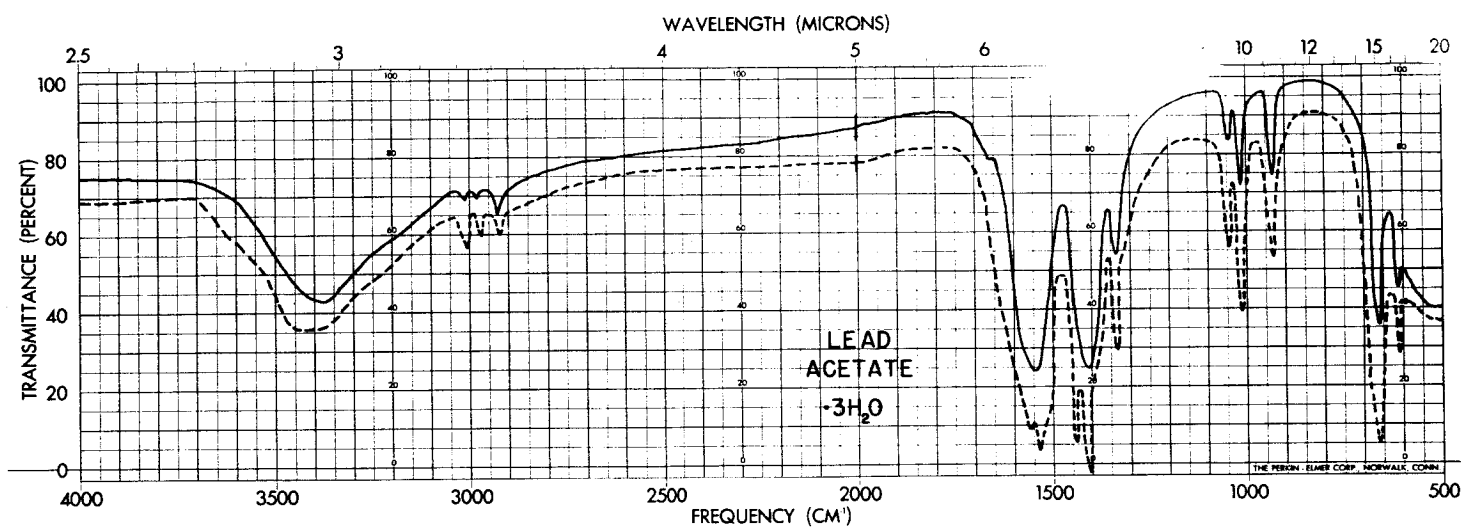
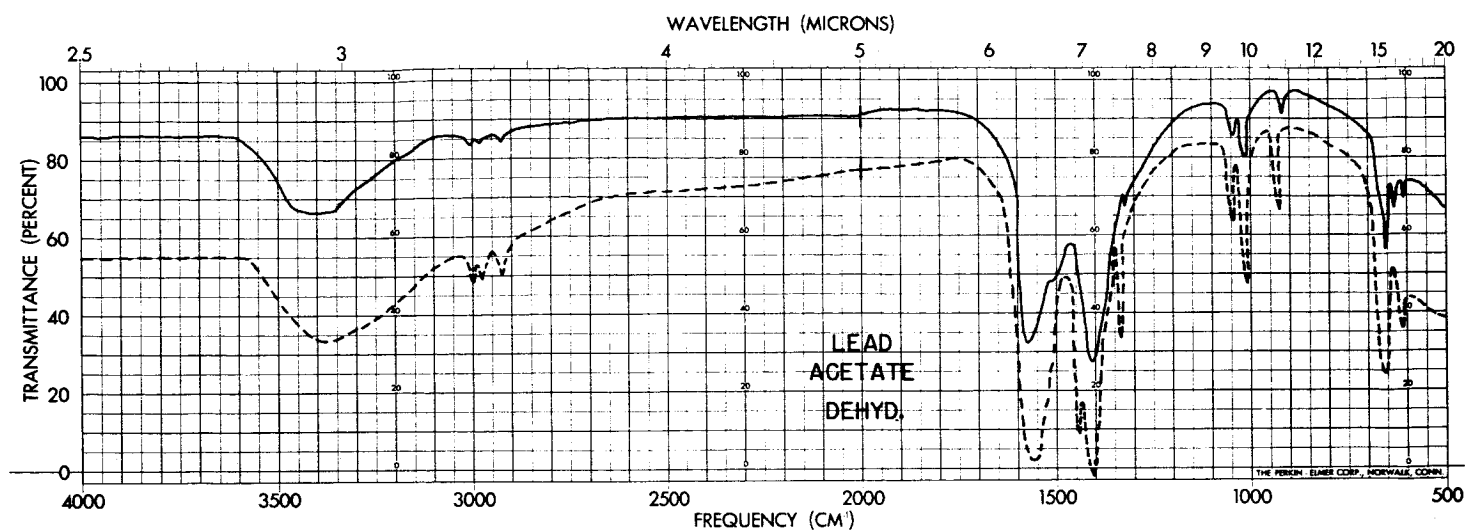


Table X

Infrared Absorption Bands of Lead Acetate Dehyd.,  $.3\text{H}_2\text{O}$  and  $.3\text{D}_2\text{O}$ 

Lead Acetate Dehyd.		Lead Acetate $.3\text{H}_2\text{O}$		Lead Acetate $.3\text{D}_2\text{O}$		Assign.
Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	
3005 vw	2998 vw	3400 bm	3425 bm			b
2980 vw	2975 vw	3010 vw	3003 vw	3002 vw	3004 w	c
2926 w	2922 vw	2980 vw	2970 vw	2970 vw	2976 w	c
		2930 w	2920 vw	2925 vw	2924 w	d
				2550 bm	2495 bm	f
		1660 w				g
1575 s	1560 s		1562 s		1554 bs	h
1514 s		1545 s	1544 s	1540 bs		h
	1440 s	1483 w	1440 s			i
1405 s	1403 s	1408 s	1406 s	1405 s	1405 s	j
1325 w	1337 w	1336 w	1336 w	1342 w	1342 m	k
				1210 m		m
1042 w	1046 w	1044 w	1046 w	1045 w	1048 w	n
1012 m	1015 m	1014 m	1014 m	1016 m	1018 m	n
924 w	929 w	932 m	932 m	935 m	934 m	o
656 s	656 s	658 s	661 s	656 s	660 s	s
632 m						s
614 m	612 m	614 m	614 m	615 m	615 m	t
461 m	460 m	464 m	464 w	466 m	465 m	x
	419 sh					v
	400 sh					v
	386 bs					v
309 m		309 m	309 w	310 m	309 m	v
299 m	300 w	299 m	301 w	300 m	300 m	v
282 m	282 w	282 m	282 m	283 m	282 m	v
273 m	273 w	273 m	274 m	274 m	274 m	v

Figure 20

Infrared Spectra of Sodium Acetate at  
Room Temperature and Liquid Nitrogen  
Temperature in the (4000-500  $\text{cm}^{-1}$ ) Region

\_\_\_\_\_ = Room Temperature

----- = Liquid Nitrogen Temperature



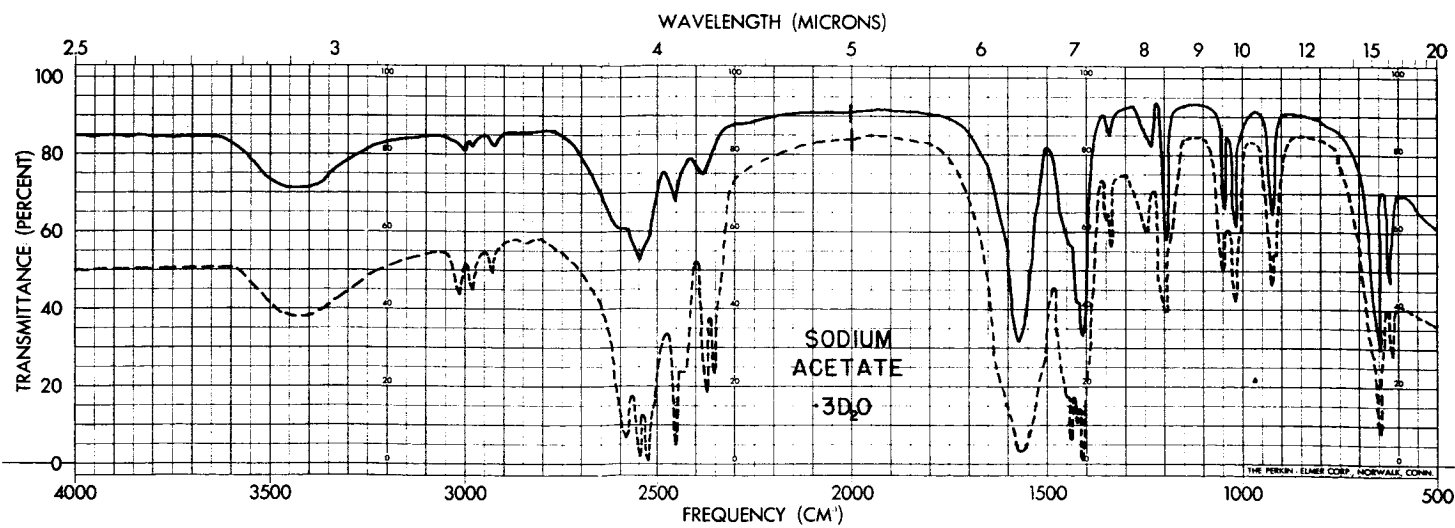
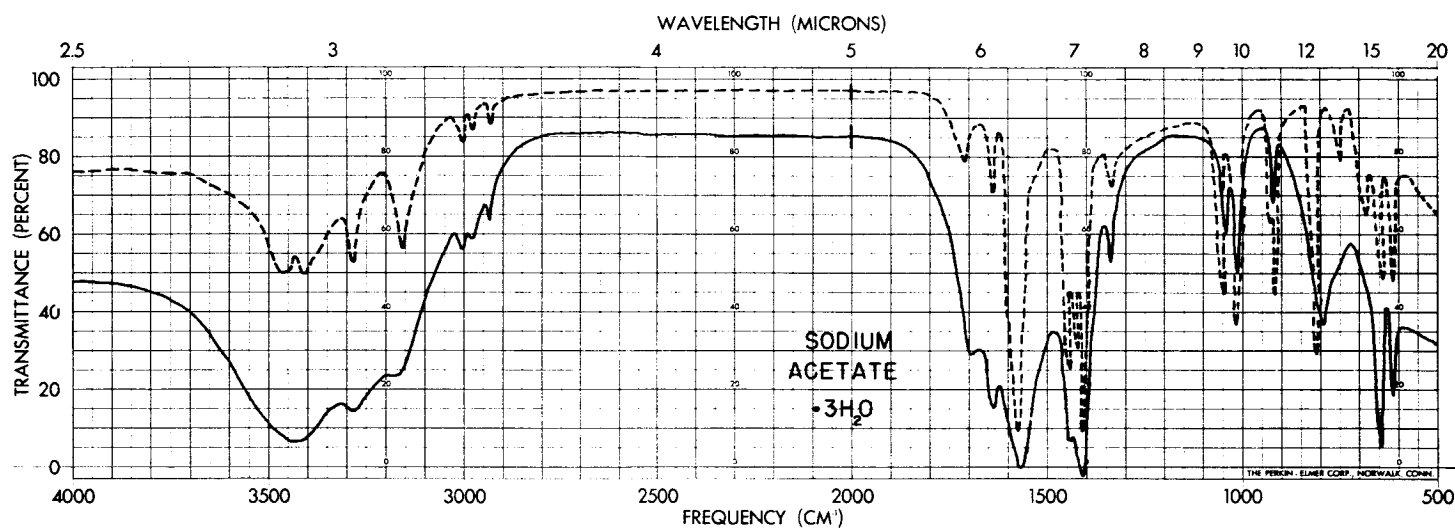
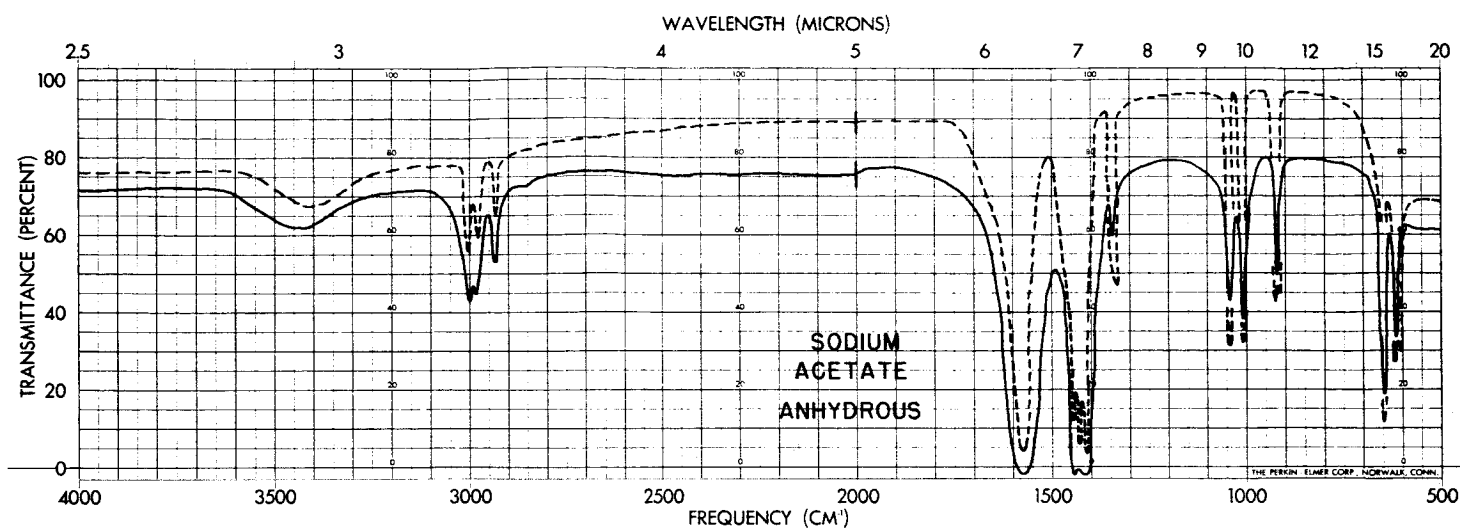


Table XI

Infrared Absorption Bands of Sodium Acetate Dehyd.,  $.3\text{H}_2\text{O}$  and  $.3\text{D}_2\text{O}$ 

Sodium Acetate Dehyd.		Sodium Acetate $.3\text{H}_2\text{O}$		Sodium Acetate $.3\text{D}_2\text{O}$		Assgn.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
			3468 s			b
		3430 bs	3415 s			b
		3285 s	3285 s			b
		3175 s	3158 s			b
2999 w	3002 w	3002 w	3002 w	3000 w	3013 vw	c
2984 w	2976 w	2978 vw	2978 vw	2980 vw	2980 vw	c
2935 w	2931 w	2935 w	2931 w	2925 w	2930 vw	d
				2590 sh	2580 s	f
				2548 bs	2546 s	f
					2527 s	f
				2451 s	2451 s	f
				2384 m	2371 m	f
					2351 m	f
		1695 m	1710 m			g
		1635 s	1639 s			g
1575 s	1575 s	1575 s	1578 s	1575 s	1574 s	h
			1488 vw		1446 sh	y
1442 s	1444 s	1442 bs	1441 s	1440 sh	1440 s	i
	1424 s		1426 s	1424 sh	1430 s	i
1415 s	1408 s	1408 bs	1407 s	1410 s	1409 s	j
1345 w					1346 w	k
		1338 w		1340 w	1340 w	k
	1332 w		1334 w		1334 vw	k
				1233 w	1244 w	m
				1196 m	1197 m	m
1042 m	1043 m	1042 m	1045 m	1048 m	1049 m	n
1012 m	1011 m	1014 m	1018 m	1017 m	1018 m	n
924 m	926 w		927 w	925 m	928 m	o
	922 m	922 m	921 m		923 vw	o
		795 bm	816 s			p
			748 w			p
			683 w			s
646 s	647 s	642 s	642 m	647 s	643 s	s
617 m	621 m	617 m	622 m	623 m	624 w	t
	613 w					t
			563 s	565 w	577 vw	u
		525 bs	538 s		526 w	u
			513 vw			u
	465 m	473 w	472 w		476 w	x
461 m	459 m			459 w		x
311 w	307 w	304 w	300 w	308 w		v
297 w	298 w	298 w	293 w	293 w	295 vw	v
282 w	282 w	284 w	284 w	282 w	283 w	v
273 w		273 w	272 w	273 w	271 w	v

coordinated water. Coordinated water absorptions in the cesium bromide region at approximately  $525\text{ cm}^{-1}$  are probably due to the librational water modes. The complete spectra of anhydrous, trihydrated, and trideuterated sodium acetate in the 2.5 to 40 micron region are presented in Table XI with band assignments being given.

## 2. Infrared Spectra of Lead and Sodium Acetates at Liquid Nitrogen Temperature ( $4000\text{-}250\text{ cm}^{-1}$ )

a. Lead acetate. The infrared spectra of lead acetate dehydrated,  $.3\text{H}_2\text{O}$ , and  $.3\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) in the 2.5 to 20 micron region in Figure 19. All absorptions in the 2.5 to 40 micron region are tabulated in Table X. As can be seen, lowered temperature has little effect on the coordinated water absorptions in lead acetate  $.3\text{H}_2\text{O}$ . The broad peak characteristic of the  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  stretching vibration shifts position slightly on cooling, but does not show any evidence of structure.

b. Sodium acetate. The infrared spectra of anhydrous sodium acetate and its hydrated and deuterated compounds are shown at liquid nitrogen temperature (broken lines) in Figure 20 from 2.5 to 20 microns. Absorption bands in these complexes from 2.5 to 40 microns are tabulated in Table XI along with band assignments and intensity data. Low temperature has a substantial effect on the spectra of sodium acetate  $.3\text{H}_2\text{O}$

and  $.3D_2O$ . The  $H_2O$  stretching absorption, although showing some structure at room temperature, splits into four well-defined peaks at liquid nitrogen temperature. From observing the spectrum of sodium acetate  $.3D_2O$  in the  $D_2O$  stretching region, four peaks are evident at room temperature, with the three lower energy peaks each splitting into a doublet at liquid nitrogen temperature, thus accounting for seven distinguishable absorptions in the  $D_2O$  stretching region. These bands are characteristic of the hydrogen bonded coordinated water molecules. The wagging, twisting, or rocking mode at  $795\text{ cm}^{-1}$  at room temperature in sodium acetate  $.3H_2O$  splits into a doublet ( $748$  and  $816\text{ cm}^{-1}$ ) upon cooling to liquid nitrogen temperature. The  $H_2O$  librational modes in the cesium bromide region show more structure at low temperature.

### 3. Acetate Vibrations

As stated previously, acetate vibrations in anhydrous sodium acetate have been studied by other investigators at both room temperature and at  $85^\circ K$ . No work has been published concerning sodium acetate  $.3D_2O$ , however. Acetate frequencies are tabulated at room and liquid nitrogen temperatures for the anhydrous,  $.3H_2O$  and  $.3D_2O$  compounds of sodium acetate in the sodium chloride and cesium bromide regions in Table XI, and the same data is given for lead acetate in Table X. Generally all acetate frequencies sharpen and intensify upon progressing

from room temperature to liquid nitrogen temperature. It is interesting to again note the room temperature absorption at  $1300-1500\text{ cm}^{-1}$  which shows essentially only two major absorptions and a shoulder in this region. At liquid nitrogen temperature, however, four major sharp absorptions are split out, which are indicative of the symmetric  $\text{CO}_2$  stretching and asymmetric and symmetric  $\text{CH}_3$  deformation frequencies in sodium acetate. Acetate frequencies in lead acetate are analogous to those of sodium acetate.

Lead and sodium acetates exhibit generally four absorptions in the  $250-311\text{ cm}^{-1}$  segment of the cesium bromide region. Since previous investigations by other workers extend to only about  $350\text{ cm}^{-1}$  in sodium acetate and no infrared data has been available for lead acetate previously, these absorptions are new. Since they appear in both lead and sodium acetates in the dehydrated, hydrated, and deuterated compounds, they are not coordinated water absorptions. These absorptions are analogous to those found in nickel, cobalt, magnesium, and manganese acetates and do not appear to sharpen or intensify at liquid nitrogen temperature and are tentatively assigned as librational modes of the acetate molecule within the crystal structure.

#### 4. Discussion of the Bonding.

a. Lead acetate. Lead acetate  $\cdot 3\text{H}_2\text{O}$  exhibits only  $\text{H}_2\text{O}$  stretching and bending vibrations and gives no infrared

evidence of other coordinated water absorptions in either the sodium chloride or cesium bromide regions. The  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching regions show no evidence of splitting of the broad hydrogen bonded water absorptions at either room temperature or at liquid nitrogen temperature. Since there is no X-ray data available on the structure of lead acetate, the infrared data presented can give only an indication as to the nature of the bonding. No absorptions were found that were assignable to metal-oxygen vibrations. No free  $\text{H}_2\text{O}$  absorptions are found and it can be assumed that all water molecules are hydrogen bonded in the structure of lead acetate.  $\cdot 3\text{H}_2\text{O}$ . The metal-oxygen and metal-water bonds show no evidence of covalent character in this complex. Since there was no splitting of the  $\text{H}_2\text{O}$  stretching absorptions, little can be said concerning types of hydrogen bonds. There is no infrared evidence for covalent character of the ligands bonded to the metal in lead acetate.

b. Sodium acetate. From the infrared analysis of sodium acetate  $\cdot 3\text{H}_2\text{O}$  and  $\cdot 3\text{D}_2\text{O}$  it is shown that there are no free water protons present as were found in nickel, cobalt, and magnesium tetrahydrate acetates. All water molecules in the sodium acetate  $\cdot 3\text{H}_2\text{O}$  structure are involved in some form of hydrogen bonding. This trihydrate differs from lead acetate  $\cdot 3\text{H}_2\text{O}$  since the infrared spectra of sodium acetate  $\cdot 3\text{H}_2\text{O}$  and  $\cdot 3\text{D}_2\text{O}$  show pronounced splitting of the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching

absorptions, showing different types of hydrogen bonded water protons present. Since sodium acetate  $\cdot 3\text{H}_2\text{O}$  shows a coordinated water absorption in the  $700\text{--}900\text{ cm}^{-1}$  region and also librational water absorptions in the cesium bromide region, there probably is some covalent character attached to the metal-water bonds. No absorptions were found assignable to a metal-oxygen vibration. Infrared evidence does indicate the possibility of both intra- and inter- molecular hydrogen bonding being of importance in the structure of sodium acetate  $\cdot 3\text{H}_2\text{O}$ .

### C. Dihydrate Acetates

1. X-ray Diffraction Data. From the X-ray analysis of lithium acetate  $\cdot 2\text{H}_2\text{O}^2$  and zinc acetate  $\cdot 2\text{H}_2\text{O}^{79}$ , space group and unit cell dimensions are tabulated in Table XII. No X-ray data is available for cadmium acetate  $\cdot 2\text{H}_2\text{O}$ .

Table XII

X-ray Data for Lithium and Zinc Dihydrate Acetates

	Space Group	Unit Cell Dimensions*				Formula Units per Unit Cell
		a	b	c	$\beta$	
$\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$	Cmm2	6.86	11.49	6.59	---	4
$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	C2/c	14.50	5.32	11.02	$100^\circ 0'$	4

\* in Angstroms

a. Bonding and structure of lithium acetate  $.2\text{H}_2\text{O}$ .

From X-ray diffraction data Amirthalingham and Pabmanabhan<sup>2</sup> state that lithium acetate  $.2\text{H}_2\text{O}$  belongs to the orthorhombic class and exhibits a "two dimensional sheet" structure. The acetate ions are separated and linked by weak hydrogen bonds of the water molecules (hydrogen bond linkage 3.08 and 3.14A) which account for the low melting point of the crystal.

Lithium is surrounded by six oxygens, four of which belong to the acetate ions and the two other to the water molecules, the lithium-oxygen (acetate) distance being 2.27A and the lithium-water distance being 2.57A.

b. Bonding and structure of zinc acetate  $.2\text{H}_2\text{O}$ .

From X-ray analysis van Niekerk, Schoening, and Talbot<sup>79</sup> show that crystals of zinc acetate  $.2\text{H}_2\text{O}$  are monoclinic and that the six nearest neighbors of a zinc ion are four oxygen atoms at distances of 2.17 and 2.18A and two water molecules at distances of 2.14A. These six bonds are probably mainly ionic in character. The six atoms form a greatly distorted octahedron around the zinc ion. The degree of distortion is probably accounted for by the O-O distance (2.21A) of the acetate group which is much too short to allow for formation of a regular octahedron. The two acetate groups are separately planar, the angle between their planes being 85 degrees. Firm hydrogen bonds of length 2.49A exist between the two water molecules of one unit



which are bonded to the two oxygen atoms of the acetate group immediately above. Adjacent columns of formula units are linked in the following manner. The two water molecules belonging to a unit in one reference column are bonded to the two oxygen atoms of two units belonging to the two columns which are adjacent to the reference column. These are hydrogen bonds of length 2.74Å.

From the above discussion it is clear that hydrogen bonds firmly link the units in the structure in such a manner as to form effectively "two dimensional sheets". This sheet-like nature of the zinc acetate structure accounts for its stacked plate-like crystal habit, the softness, and the marked cleavage of the crystals.

## 2. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Room Temperature (4000-250 $\text{cm}^{-1}$ ).

a. Cadmium acetate. Cadmium acetate  $\cdot 2\text{H}_2\text{O}$  is characterized by a broad absorption at  $3450 \text{ cm}^{-1}$  which shifts to  $2535 \text{ cm}^{-1}$  in cadmium acetate  $\cdot 2\text{D}_2\text{O}$  and which is absent from the spectrum of dehydrated cadmium acetate and is assigned as the  $\text{H}_2\text{O}$  stretching vibration of the coordinated water molecules. The  $\text{H}_2\text{O}$  bending vibration of the coordinated water was not observed as a distinct absorption in cadmium acetate  $\cdot 2\text{H}_2\text{O}$ , but appeared at  $1204 \text{ cm}^{-1}$  in the spectrum of cadmium acetate  $\cdot 2\text{D}_2\text{O}$ . No other absorptions due to coordinated water were found in either the  $700\text{-}900 \text{ cm}^{-1}$  or cesium bromide regions. The infrared

spectra of cadmium acetate dehyd.,  $.2\text{H}_2\text{O}$  and  $.2\text{D}_2\text{O}$  are shown in the 2.5 to 20 micron region in Figure 21 and all the observed absorption bands in the 2.5 to 40 micron region are tabulated with assignments in Table XIII.

b. Lithium acetate. Lithium acetate  $.2\text{H}_2\text{O}$  has  $\text{H}_2\text{O}$  stretching vibrations at  $3170\text{--}3400\text{ cm}^{-1}$  which shift to  $2330\text{--}2520\text{ cm}^{-1}$  in the deuterated hydrate and are absent from the spectrum of dehydrated lithium acetate. The dihydrate also has an absorption at  $1710\text{ cm}^{-1}$  which shifts to  $1197\text{--}1248\text{ cm}^{-1}$  in the deuterated hydrate and is absent in the spectrum of dehydrated lithium acetate and is assigned as the  $\text{H}_2\text{O}$  bending vibration of the coordinated water molecules. Lithium acetate  $.2\text{H}_2\text{O}$  has a coordinated water absorption at  $858\text{ cm}^{-1}$  which shifts in the spectrum of lithium acetate  $.2\text{D}_2\text{O}$  and is absent from the spectrum of dehydrated lithium acetate and is assigned as an  $\text{H}_2\text{O}$  wagging, twisting, or rocking mode. The dihydrate also gives rise to absorption in the far infrared which is probably due to the librational modes of the coordinated water. The infrared spectra of lithium acetate dehyd.,  $.2\text{H}_2\text{O}$  and  $.2\text{D}_2\text{O}$  from 2.5 to 20 microns are presented in Figure 22 and all absorption bands in these compounds from 2.5 to 40 microns are tabulated with assignments in Table XIV.

c. Zinc acetate. The  $\text{H}_2\text{O}$  stretching vibration in

Figure 21  
 Infrared Spectra of Cadmium Acetate at Room  
 Temperature and Liquid Nitrogen Temperature  
 in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
 \_\_\_\_\_ = Room Temperature  
 ----- = Liquid Nitrogen Temperature

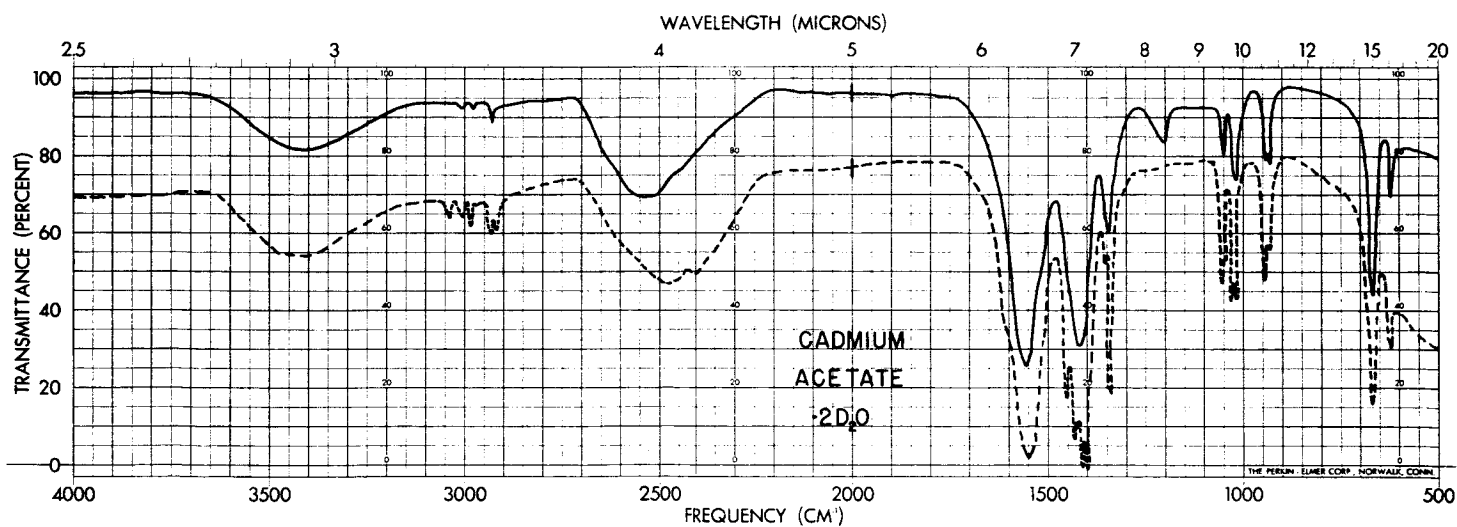
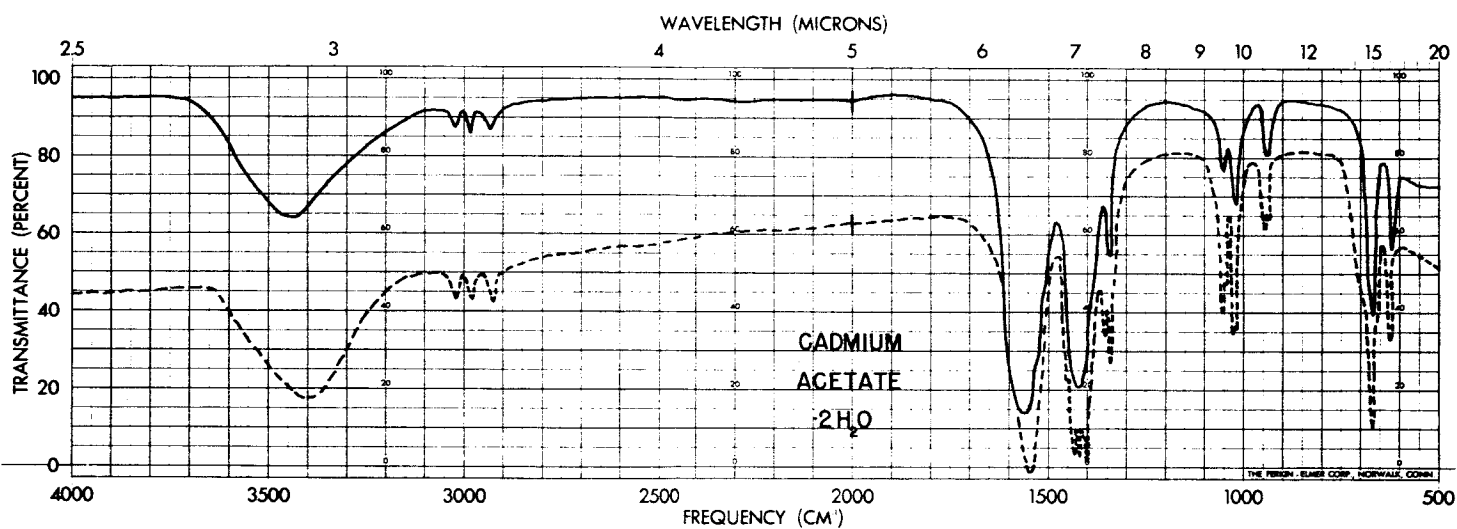
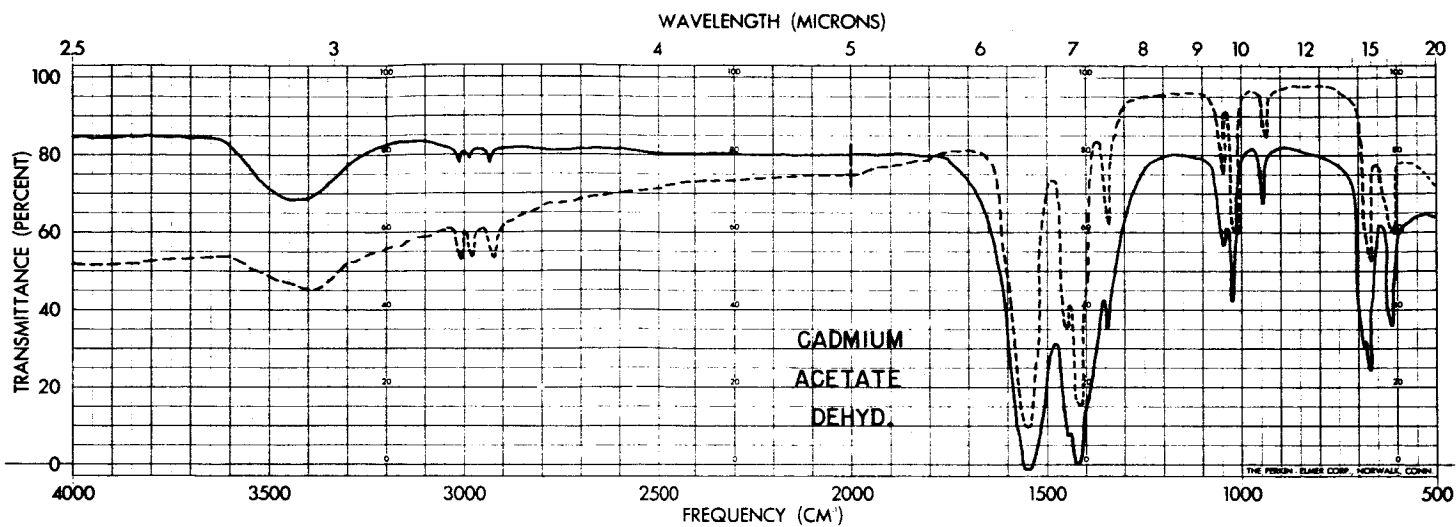


Table XIII

Infrared Absorption Bands of Cadmium Acetate Dehyd.,  $.2\text{H}_2\text{O}$  and  $.2\text{D}_2\text{O}$ 

Cadmium Acetate Dehyd.		Cadmium Acetate. $.2\text{H}_2\text{O}$		Cadmium Acetate. $.2\text{D}_2\text{O}$		Assign
Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	
		3450 bm	3420 bm			b
3010 vw	3008 vw	3020 vw	3020 vw	3005 vw	3038 w	c
2985 vw	2978 vw	2982 vw	2980 vw	2978 vw	3006 w	c
2932 vw	2923 vw	2932 vw	2925 vw	2929 w	2987 w	c
					2933 w	d
					2921 vw	d
				2535 bm	2480 bm	f
					2405 bm	f
1550 bs	1549 s	1560 bs	1545 s	1555 bs	1550 s	h
1442 s	1447 s		1456 m		1456 m	i
			1431 s		1432 s	i
1423 bs	1412 s	1420 s	1421 s	1420 s	1423 s	i
			1412 s		1413 s	j
			1406 s		1407 s	j
			1358 w		1358 w	k
1341 w	1342 m	1343 w	1346 m	1346 w	1347 m	k
				1204 w		m
			1057 m		1058 m	n
1048 w	1049 w	1050 w	1051 w	1049 w	1051 m	n
			1029 m		1031 m	n
1024 m	1018 m	1018 m	1024 m	1018 m	1024 m	n
947 w		941 w	944 w	941 m	945 m	o
	938 w	937 w	937 w	936 m	938 m	o
683 s						s
670 s	670 s	668 s	671 s	669 s	669 s	s
615 m	620 m	620 m	625 m	622 m	625 m	t
			473 m	475 vw	474 vw	x
463 w	463 w	464 w	464 m	467 w	465 w	x
313 vw	308 vw	310 m	311 m	311 m	310 m	v
298 w	299 m	299 m	299 m	299 m	299 m	v
282 m	281 m	282 m	282 m	282 m	282 m	v
273 m	274 m	273 m	274 m	274 m	274 m	v

Figure 22  
Infrared Spectra of Lithium Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

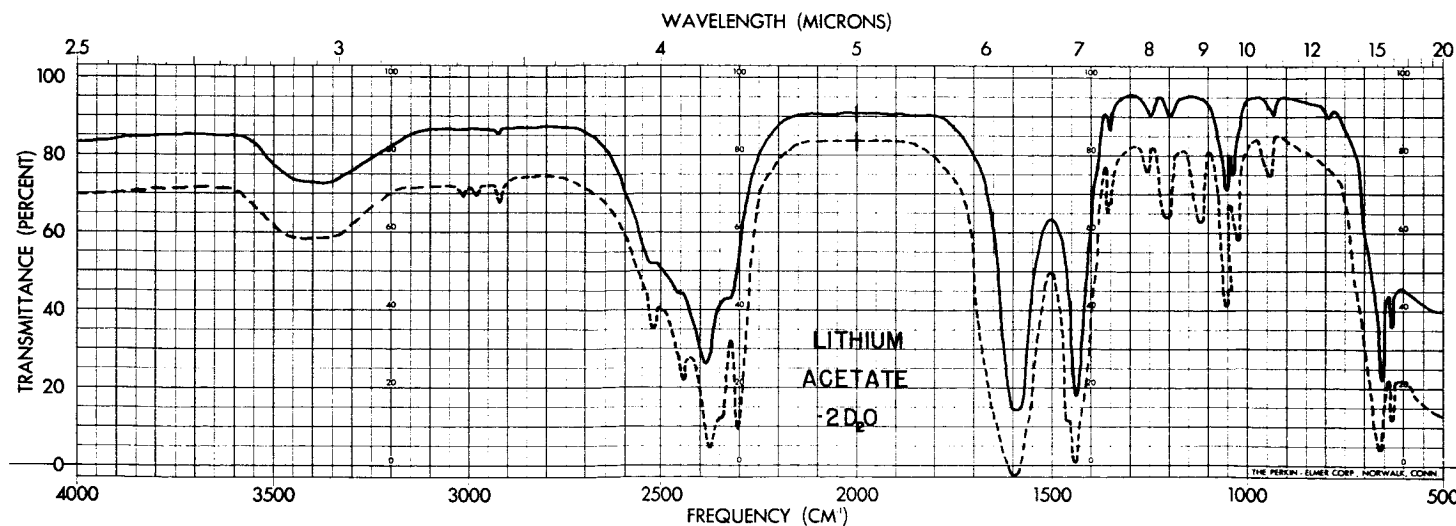
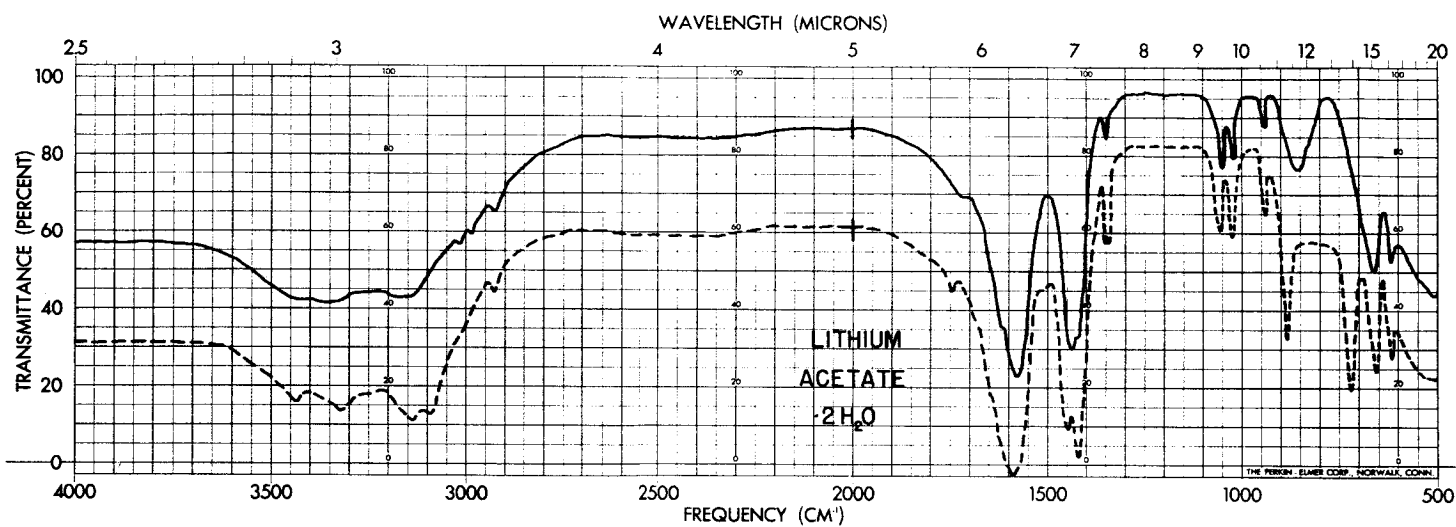
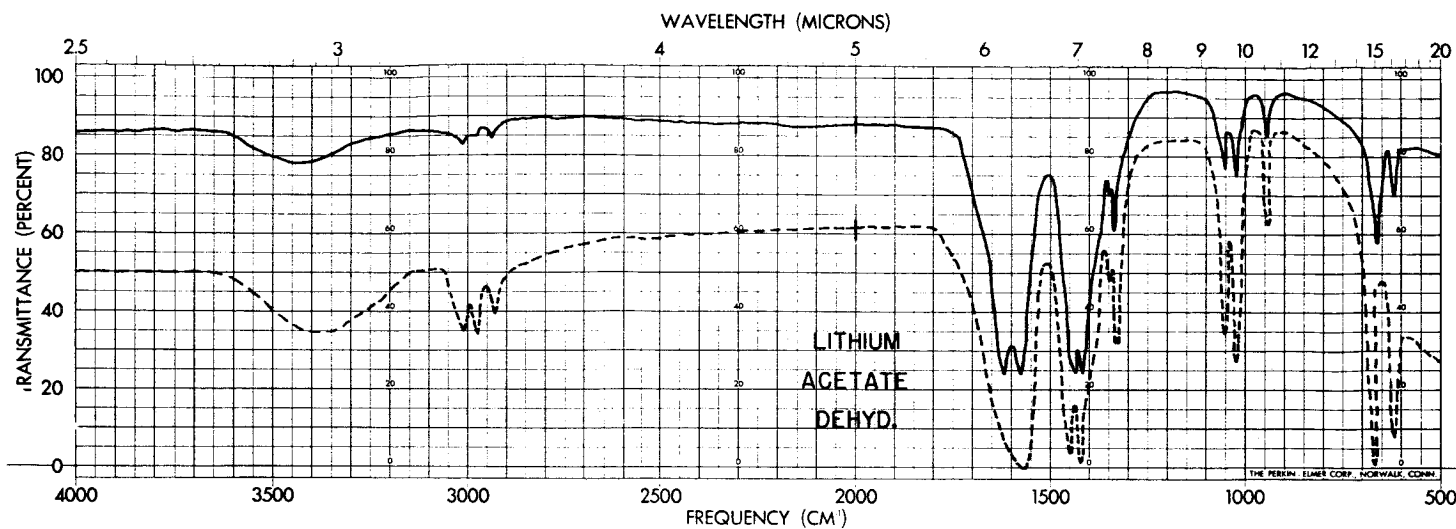


Table XIV

Infrared Absorption Bands of Lithium Acetate Dehyd., .2H<sub>2</sub>O and .2D<sub>2</sub>O

Lithium Acetate Dehyd.		Lithium Acetate .2H <sub>2</sub> O		Lithium Acetate .2D <sub>2</sub> O		Assign
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3400 bs	3435 m			b
			3320 m			b
		3170 bs	3135 m			b
			3090 m			b
3015 vw	3010 vw	3015 vw			3012 vw	c
2978 vw	2978 vw	2985 vw			2980 vw	c
2938 vw	2930 vw	2935 vw	2928 vw		2925 vw	d
				2520 m	2518 m	f
				2450 sh	2440 m	f
				2388 s	2375 s	f
				2330 sh	2351 sh	f
					2301 s	f
		1710 w	1742 w			g
1618 s		1622 s				h
1578 s	1575 s	1580 s	1590 s	1590 s	1593 s	h
					1462 sh	y
1435 s	1448 s	1438 s	1447 s	1442 bs	1441 s	i
1418 s	1426 s	1422 s	1420 s			j
1347 w	1346 w	1348 w	1351 w	1350 w	1358 w	k
1341 m	1340 m		1341 w		1353 sh	k
	1338 m					k
				1248 w	1256 w	m
					1207 m	m
				1197 w	1120 m	m
1050 w	1051 m	1050 w	1054 w	1054 m	1054 m	n
			1051 w		1048 m	n
1022 w	1022 m	1023 w	1026 w	1038 w	1025 w	n
943 w	944 w	940 w	938 w	933 vw	942 w	o
		858 w	887 m			p
			721 s	790 vw		p
665 s	669 s	664 s	657 s	657 s	661 s	s
620 m	620 m	620 m	617 s	635 m	635 m	t
				568 m	569 m	u
					543 w	u
				524 w	532 w	v
	519 sh		511 s			v
493 bs	492 m	494 m				x
458 w	450 bs					x
439 bs		424 w	423 s	427 vw	418 vw	x
408 s	414 sh			407 w	408 w	x
391 m		387 vw		380 vw	375 vw	v
362 m	369 bm	355 vw	365 s	360 w	360 s	v
		344 w		345 w	346 vw	u
	307 w	316 vw				v
299 w	299 w	302 m	303 m	298 bm	296 bm	v
290 vw	287 vw		291 w		292 bm	v
285 w	282 w	285 vw	285 vw	286 vw	283 vw	v
274 w	274 w	275 bm	276 m	273 bm	272 bm	v
		264 vw				v

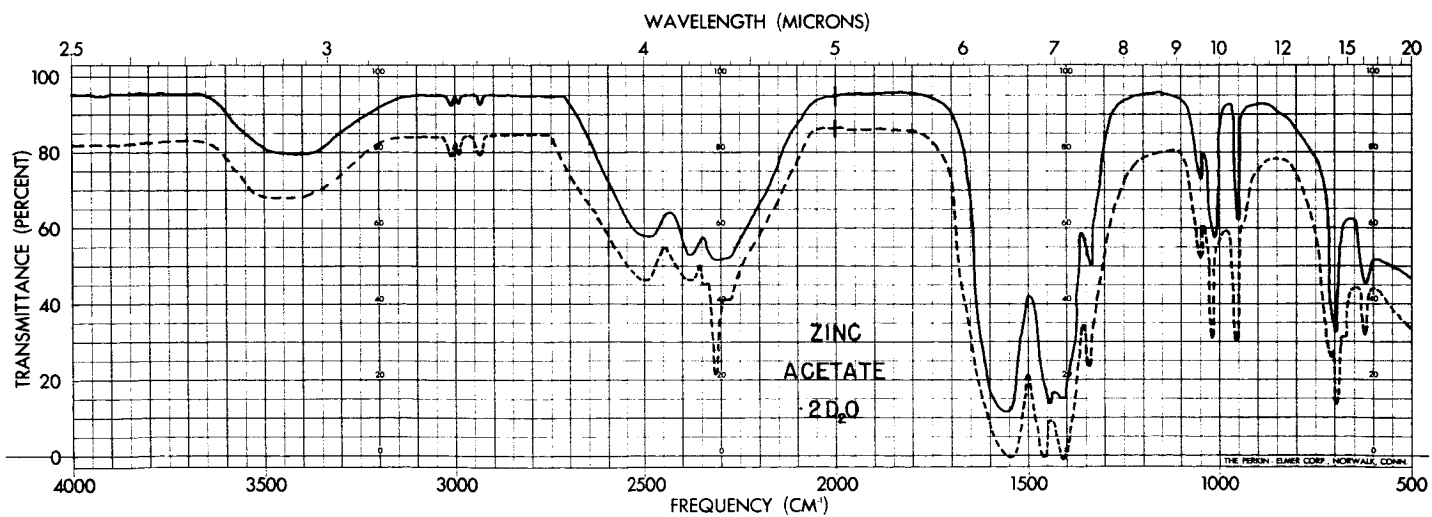
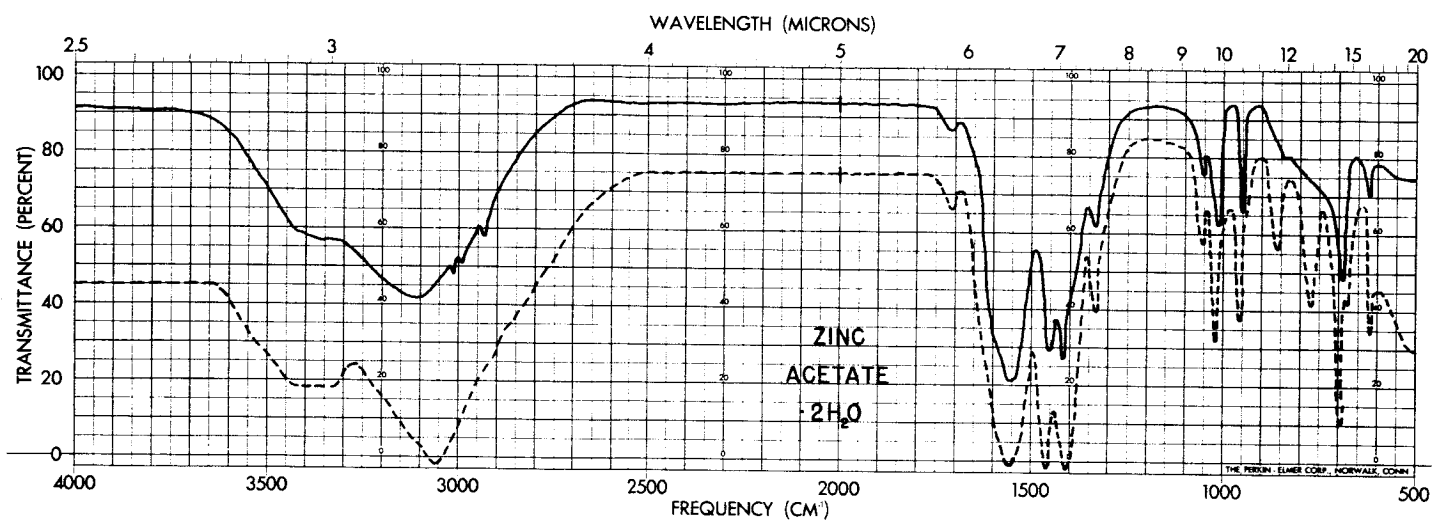
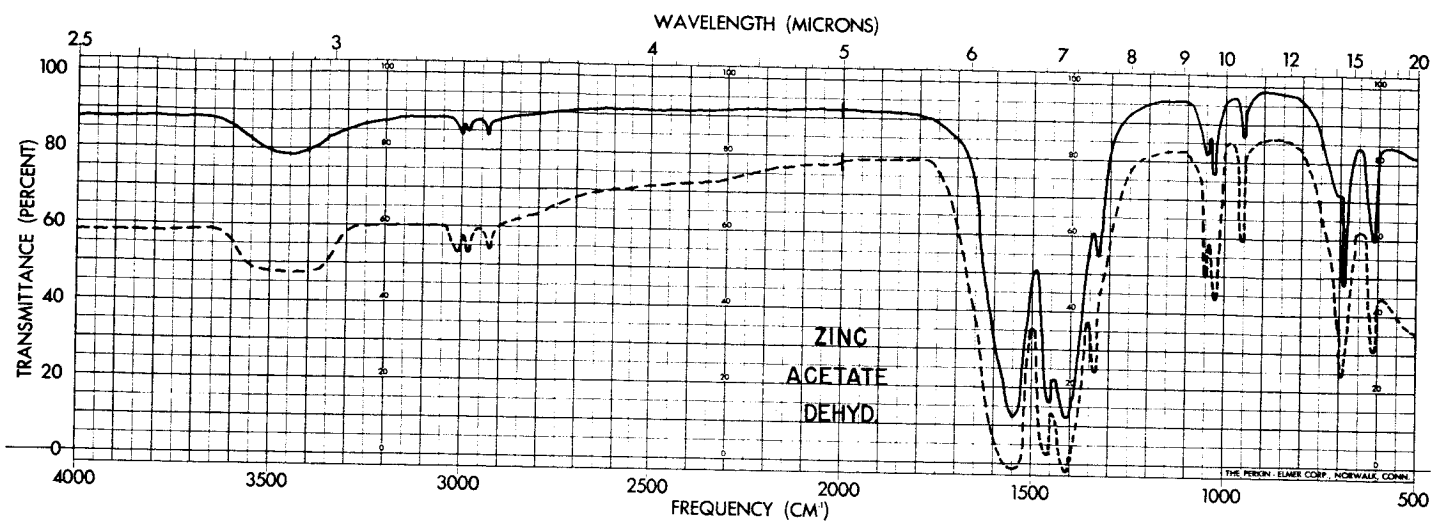


zinc acetate  $\cdot 2\text{H}_2\text{O}$  occurs at  $3125\text{--}3385\text{ cm}^{-1}$  and shifts to  $2300\text{--}2500\text{ cm}^{-1}$  in zinc acetate  $\cdot 2\text{D}_2\text{O}$  and is absent from the spectrum of dehydrated zinc acetate. The  $\text{H}_2\text{O}$  bending vibration occurs at  $1710\text{ cm}^{-1}$  in the dihydrate and is absent in the spectra of dehydrated and deuterated compounds. The  $\text{D}_2\text{O}$  bending vibration in the deuterated hydrate is apparently very weak and was not detected in the spectrum of zinc acetate  $\cdot 2\text{D}_2\text{O}$ . Zinc acetate  $\cdot 2\text{H}_2\text{O}$  gives rise to an absorption at  $835\text{ cm}^{-1}$  which shifts in the spectrum of the deuterated hydrate and is absent from the spectrum of dehydrated zinc acetate and is assigned as an  $\text{H}_2\text{O}$  rocking, twisting, or wagging vibration of the coordinated water. Water absorption in the cesium bromide region is assigned as being due to librational modes of the coordinated water molecules. The infrared spectra of zinc acetate dehyd.,  $\cdot 2\text{H}_2\text{O}$  and  $\cdot 2\text{D}_2\text{O}$  are shown from 2.5 to 20 microns in Figure 23 and the complete spectra from 2.5 to 40 microns are tabulated with assignments in Table XV.

### 3. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Liquid Nitrogen Temperature ( $4000\text{--}250\text{ cm}^{-1}$ ).

a. Cadmium acetate. The infrared spectra of cadmium acetate dehyd.,  $\cdot 2\text{H}_2\text{O}$  and  $\cdot 2\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) from 2.5 to 20 microns in Figure 21, and all absorptions from 2.5 to 40 microns are

Figure 23  
Infrared Spectra of Zinc Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature



Infrared Absorption Bands of Zinc Acetate Dehyd.  $.2\text{H}_2\text{O}$  and  $.2\text{D}_2\text{O}$ 

Zinc Acetate Dehyd.		Zinc Acetate $.2\text{H}_2\text{O}$		Zinc Acetate $.2\text{D}_2\text{O}$		Assign
Room Temp $\text{Cm}^{-1}$	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$	Room Temp $\text{Cm}^{-1}$	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$	Room Temp $\text{Cm}^{-1}$	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$	
		3385 bm	3385 bw			b
		3125 bs	3060 s			b
3000 vw	3009 vw	3011 vw	3010 vw	3010 vw	3010 vw	c
2985 vw	2983 vw	2990 vw	2985 vw	2990 vw	2990 vw	c
2935 vw	2927 vw	2935 vw	2930 vw	2935 vw	2935 vw	d
				2500 bs	2490 bs	f
				2380 bs	2378 m	f
					2347 sh	f
				2300 bs	2315 s	f
					2283 sh	f
		1710 vw	1710 vw			g
1550 bs	1550 vs	1555 bs	1545 s	1558 bs	1545 bs	h
1445 s	1460 s	1450 s	1462 s	1445 s	1458 s	i
1410 s	1412 s	1418 s	1412 s	1410 m	1411 s	j
1328 w	1337 w	1335 w	1334 w	1336 w	1341 w	k
1047 w	1050 w	1052 w	1054 w	1048 w	1050 w	n
1030 m	1024 m	1016 m	1020 m	1014 m	1021 m	n
953 w	956 w	952 m	956 m	952 m	957 m	o
		835 w	860 w			p
			774 w			p
701 w					706 m	s
691 s	695 s	691 s	694 s	697 s	698 s	s
			683 w		676 sh	s
612 s	613 s	621 m	621 m	620 m	622 m	t
515 m	519 w		473 vw			x
	510 vw					x
	346 s	389 bw	402 s			x
340 bs	338 sh	343 w	337 vw		346 bs	v
331 s	331 sh	331 vw	330 vw	329 vw	331 vw	v
	317 w	319 vw	312 vw	310 m	319 w	v
		314 w			312 vw	u
300 w	301 w	302 w	304 m	302 m	301 w	v
282 w	282 w	283 w	283 w	281 m	282 m	v
274 m	274 w	276 m	277 m	275 m	275 m	v

tabulated in Table XIII. The spectrum of cadmium acetate  $\cdot 2\text{H}_2\text{O}$  at liquid nitrogen temperature shows essentially only a slight shift of the broad  $\text{H}_2\text{O}$  stretching vibration from that at room temperature. The  $\text{D}_2\text{O}$  stretching region of the deuterated hydrate shows a doublet at liquid nitrogen temperature. There are no coordinated water absorptions in either the  $700\text{--}900\text{ cm}^{-1}$  or cesium bromide regions in cadmium acetate  $\cdot 2\text{H}_2\text{O}$ . Lowered temperature has no pronounced effect upon the coordinated water absorptions.

b. Lithium acetate. The spectra of lithium acetate dehyd.,  $\cdot 2\text{H}_2\text{O}$  and  $\cdot 2\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) from 2.5 to 20 microns in Figure 22, while complete spectral bands from 2.5 to 40 microns are tabulated with assignments at liquid nitrogen temperature in Table XIV. The  $\text{H}_2\text{O}$  stretching vibration, although showing some structure at room temperature, actually splits into four distinct peaks ( $3090$ ,  $3135$ ,  $3320$ , and  $3435\text{ cm}^{-1}$ ) at liquid nitrogen temperature. The  $\text{D}_2\text{O}$  stretching vibration of the deuterated hydrate shows four peaks at room temperature, but these intensify and sharpen at liquid nitrogen temperature with four peaks and a shoulder becoming evident. The  $\text{H}_2\text{O}$  bending vibration in the dihydrate also sharpens and intensifies at low temperature. The room temperature absorption at  $858\text{ cm}^{-1}$  in the dihydrate

actually splits into a well defined doublet ( $721$  and  $887\text{ cm}^{-1}$ ) at liquid nitrogen temperature. The librational water modes in the far infrared also show a splitting at low temperature.

c. Zinc acetate. The  $\text{H}_2\text{O}$  stretching vibration in zinc acetate  $\cdot 2\text{H}_2\text{O}$  shows a broad doublet at both room and liquid nitrogen temperatures. The deuterated hydrate exhibits three peaks at room temperature in the  $\text{D}_2\text{O}$  stretching region with one of these splitting into a doublet at liquid nitrogen temperature accounting for four peaks characteristic of the hydrogen bonded water molecules. Zinc acetate  $\cdot 2\text{H}_2\text{O}$  has an absorption at  $835\text{ cm}^{-1}$  which splits into a doublet ( $774$ - $860\text{ cm}^{-1}$ ) at liquid nitrogen temperature which is characteristic of the coordinated water molecules. The spectra of zinc acetate dehyd.,  $\cdot 2\text{H}_2\text{O}$  and  $\cdot 2\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) in Figure 23 from  $2.5$  to  $20$  microns, while complete absorptions from  $2.5$  to  $40$  microns are tabulated with assignments in Table XV.

#### 4. Acetate Vibrations.

Tables XIII, XIV, and XV give acetate assignments for cadmium, lithium and zinc acetates, respectively. Acetate vibrations do not vary a great deal from acetate to acetate so that the discussions given previously for the acetate vibrations in the tri- and tetra- hydrate acetates are also applicable to the

dihydrates. It was found that some of the acetate vibrations in the dihydrates were also split into doublets at liquid nitrogen temperature. It is interesting to again note the splitting of the  $1300\text{--}1500\text{ cm}^{-1}$  absorption into the characteristic acetate frequencies at low temperature.

Essentially four absorptions were found in the  $250\text{--}300\text{ cm}^{-1}$  segment of the cesium bromide region. These absorptions were present in the dehydrated, hydrated, and deuterated hydrates of cadmium, lithium, and zinc acetates. The absorptions are not influenced by low temperature and are tentatively assigned by analogy with similar absorptions found in the other acetates, to a librational motion of the whole molecule within the crystal structure.

## 5. Discussion of the Bonding.

a. Cadmium acetate. Infrared analysis would indicate that cadmium acetate  $\cdot 2\text{H}_2\text{O}$  has no free water protons as was found in some of the tetrahydrates. Since the hydrogen bonded  $\text{H}_2\text{O}$  stretching absorption did not split at liquid nitrogen temperature, apparently there is no great difference between the hydrogen bonded water protons. Since no coordinated water absorptions were found in either the  $700\text{--}900\text{ cm}^{-1}$  or far infrared regions, there is no infrared evidence for covalent character of the metal-water bonds in cadmium acetate  $\cdot 2\text{H}_2\text{O}$ .

b. Lithium acetate. X-ray diffraction results show that lithium acetate dihydrate has a two dimensional sheet structure and that the water molecules make hydrogen bonds to the oxygen atoms of the acetate groups. The  $\text{H}_2\text{O}$  stretching region of the dihydrate and the  $\text{D}_2\text{O}$  stretching region of the deuterated hydrate show well defined splittings at liquid nitrogen temperature indicating that the hydrogen bonded water protons are involved in hydrogen bonds of different lengths. No free water protons are present in lithium acetate  $\cdot 2\text{H}_2\text{O}$ . Since wagging, twisting, or rocking modes and librational modes of the coordinated water molecules are apparent, this would indicate some degree of covalent character attached to the metal-water bonds.

c. Zinc acetate. X-ray data indicate a two dimensional sheet structure for zinc acetate  $\cdot 2\text{H}_2\text{O}$  as was found in lithium acetate  $\cdot 2\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching regions of the dihydrate and deuterated hydrate, respectively, show definite splittings at liquid nitrogen temperature, indicating different hydrogen bond lengths for the water protons. There are no free water protons present in zinc acetate  $\cdot 2\text{H}_2\text{O}$ . Coordinated water absorptions are present in both the 700-900  $\text{cm}^{-1}$  and far infrared regions indicating some degree of covalent character of the metal-water bonds. Infrared analysis indicates a similar structure for lithium and zinc dihydrate acetates.



D. Monohydrate Acetates

1. X-ray Diffraction Data. From the X-ray analysis of cupric acetate  $\cdot\text{H}_2\text{O}$ <sup>77</sup> and chromous acetate  $\cdot\text{H}_2\text{O}$ <sup>76</sup> space group and the monoclinic unit cell dimensions are presented in Table XVI.

Table XVI

X-ray Data for Cupric and Chromous Monohydrate Acetates

	Space Group	Unit Cell Dimensions*				Formula Units per Unit Cell
		a	b	c	$\beta$	
$\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$	C2/c	13.15	8.52	13.90	$117^\circ 0'$	4
$\text{Cr}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$	C2/c	13.15	8.55	13.94	$117^\circ 0'$	4

\* in Angstroms

Chromous acetate  $\cdot\text{H}_2\text{O}$  was included in the above table solely for the purpose of illustrating that this hydrate is isostructural with cupric acetate  $\cdot\text{H}_2\text{O}$ . Chromous acetate  $\cdot\text{H}_2\text{O}$  is unstable in the atmosphere and is stable only in an atmosphere of hydrogen or nitrogen, etc. For this reason chromous acetate  $\cdot\text{H}_2\text{O}$  was not studied here; instead, chromic acetate  $\cdot\text{H}_2\text{O}$  which is stable in the atmosphere, was studied. However, no X-ray data is available for chromic acetate  $\cdot\text{H}_2\text{O}$ , as is the case for calcium acetate  $\cdot\text{H}_2\text{O}$ .

a. Bonding and structure of cupric acetate  $\cdot\text{H}_2\text{O}$ .

From X-ray diffraction data van Niekerk and Schoening<sup>77</sup> state

that crystals of cupric acetate  $\cdot H_2O$  are monoclinic and apart from van der Waals forces, each molecule is linked by eight hydrogen bonds (2.82 and 2.89A) to four neighboring molecules at different levels. The distance between the copper atoms is 2.64A. This short Cu-Cu distance indicates that a metal-metal bond may exist in the structure of cupric acetate  $\cdot H_2O$ .

Four oxygen atoms, arranged approximately on a square, form the nearest neighbors of a copper atom (1.97A). In this respect the coordination resembles that normally encountered in divalent copper compounds. Perpendicularly above and below the plane containing the four oxygen atoms lies a water molecule at a distance of 2.20A and a copper atom at a distance of 2.64A, thus completing the distorted octahedral configuration about each copper atom. Further evidence of the distortion in the molecule is to be seen by comparing the Cu-Cu distance (2.64A) and the O-O distance for one acetate group (2.20A).

van Niekerk and Schroening also state that until further information becomes available no attempt will be made to explain the bonds in this unusual complex.

## 2. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Room Temperature (4000-250 $cm^{-1}$ ).

a. Calcium acetate. Calcium acetate  $\cdot H_2O$  shows absorption at 3400  $cm^{-1}$  with a shoulder at 3275  $cm^{-1}$  ( $H_2O$

stretching vibration),  $1605\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  bending vibration), shifting to  $2345\text{--}2595\text{ cm}^{-1}$  and  $1231\text{ cm}^{-1}$  respectively, upon substitution of heavy water. These absorptions disappear from the spectrum upon dehydration. No absorptions attributable to coordinated water appear in the  $700\text{--}900\text{ cm}^{-1}$  region and no well defined librational water modes are apparent in the cesium bromide region. The infrared spectra of calcium acetate dehyd.,  $\cdot\text{H}_2\text{O}$  and  $\cdot\text{D}_2\text{O}$  are shown from 2.5 to 20 microns in Figure 24 and complete absorption bands with assignments from 2.5 to 40 microns are presented in Table XVII.

b. Chromic acetate. Chromic acetate  $\cdot\text{H}_2\text{O}$  has coordinated water absorptions at  $3425\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  stretching vibration) and  $1610\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  bending frequency), shifting to  $2524\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ , respectively, upon substitution of deuterium oxide and disappear from the spectra upon dehydration. Coordinated water absorptions were not found in the  $700\text{--}900\text{ cm}^{-1}$  region in the hydrate, but absorption in the cesium bromide region at  $531\text{--}571\text{ cm}^{-1}$  is probably due to the librational water modes. The spectra of chromic acetate dehyd.,  $\cdot\text{H}_2\text{O}$  and  $\cdot\text{D}_2\text{O}$  from 2.5 to 20 microns are shown in Figure 25, while complete absorption bands with assignments from 2.5 to 40 microns are tabulated in Table XVIII.

c. Cupric acetate. Cupric acetate  $\cdot\text{H}_2\text{O}$  has

Figure 24  
Infrared Spectra of Calcium Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region

\_\_\_\_\_ = Room Temperature

----- = Liquid Nitrogen Temperature

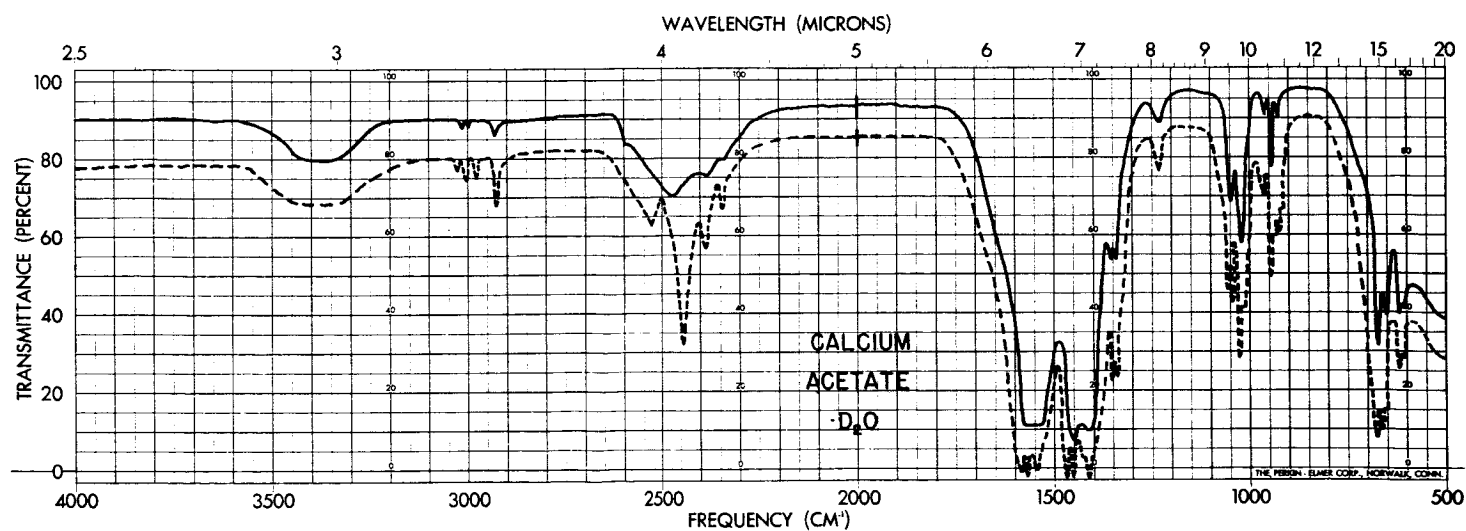
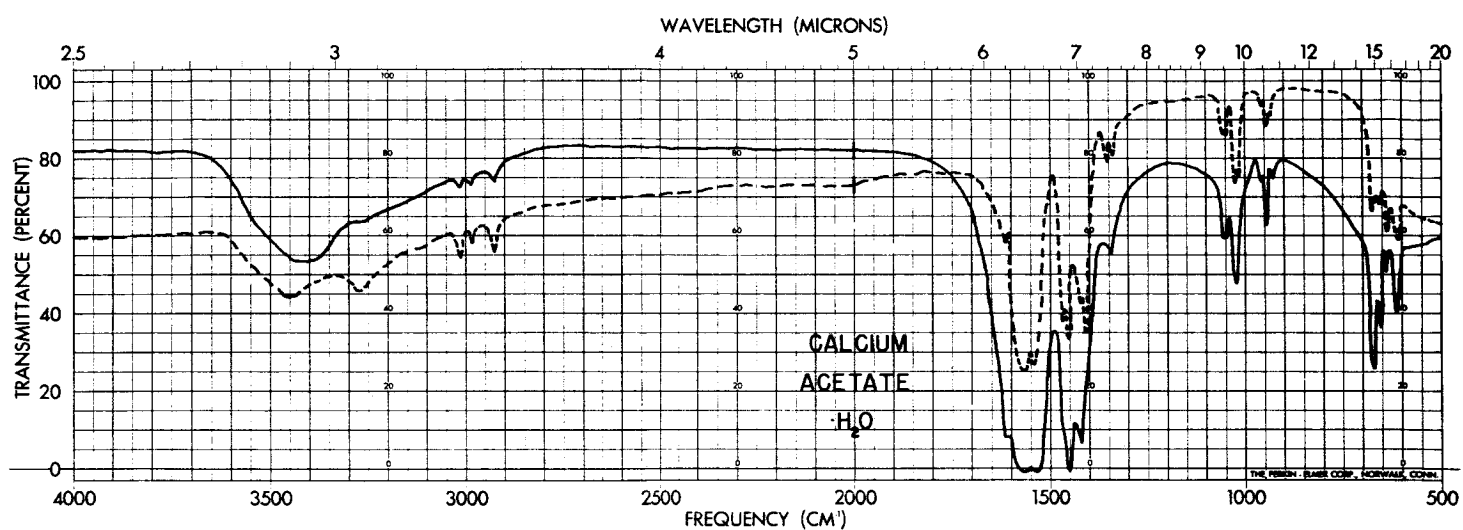
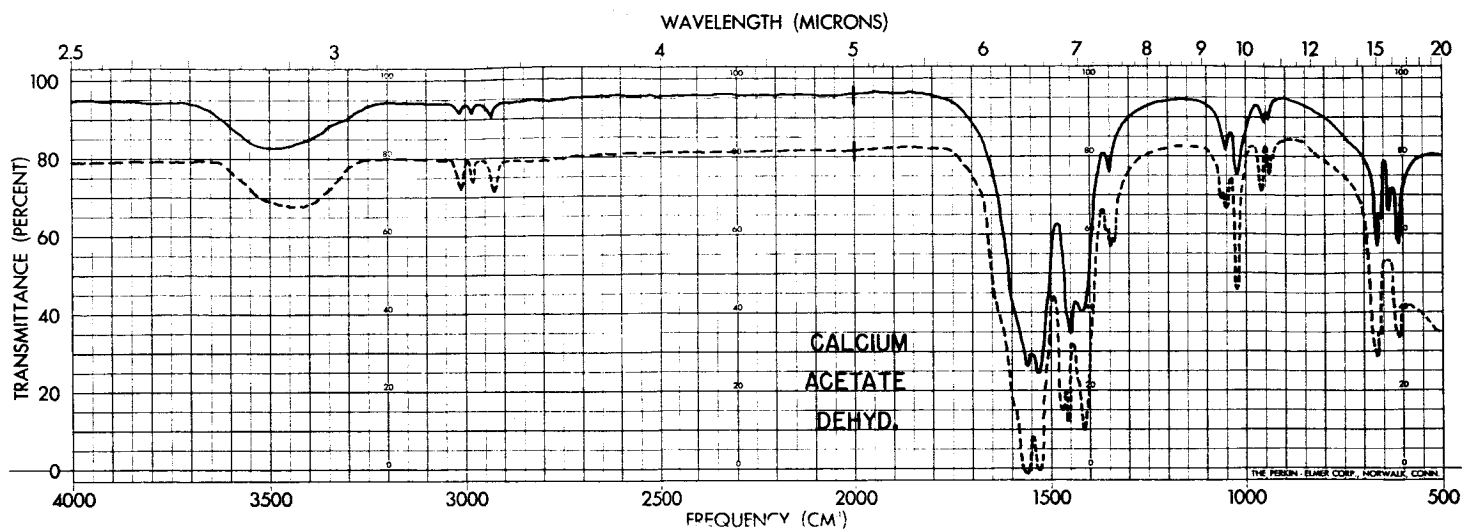


Table XVII

Infrared Absorption Bands of Calcium Acetate Dehyd., . H<sub>2</sub>O and . D<sub>2</sub>O

Calcium Acetate Dehyd.		Calcium Acetate .H <sub>2</sub> O		Calcium Acetate.D <sub>2</sub> O		Assgn.
Room Temp Cm. <sup>-1</sup> I	Liq.N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq.N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3400 bm	3450 m			b
			3275 m			b
3015 vw	3010 vw	3015 vw	3015 vw	3015 vw	3026 vw	c
					3006 vw	c
2985 vw	2982 vw	2985 vw	2985 vw	2999 vw	2978 vw	c
2934 vw	2926 vw	2934 vw	2925 vw	2930 vw	2929 vw	d
				2595 m	2530 m	f
				2470 m	2442 s	f
				2382 m	2386 m	f
				2345 m	2348 m	f
		1605 vw	1613 vw			g
					1583 sh	h
1562 bs	1560 s	1570 bs	1565 s	1560 bs	1570 s	h
1532 s	1530 s	1535 s	1545 s		1546 sh	h
	1470 s		1468 s		1469 s	i
1450 s	1460 s	1450 s	1456 s	1450 s	1455 s	i
1418 s	1415 s	1420 s	1423 w	1415 m	1425 sh	j
			1411 s		1414 s	j
	1356 vw		1352 w	1355 w	1355 w	k
1350 w	1348 w	1345 w				k
	1343 w		1340 w	1343 w	1343 w	k
				1231 w	1234 w	m
	1060 w		1052 w		1058 w	n
1050 w	1050 w	1050 w	1047 w	1048 w	1048 w	n
			1028 m		1030 m	n
1022 m	1025 m	1022 m	1022 m	1022 m	1025 m	n
					965 w	o
952 w	958 w	958 w	955 vw	960 w	958 vw	o
					948 m	o
943 w	942 w	944 w	946 w	945 m	943 m	o
	937 vw	929 vw	941 vw	929 w	929 w	o
					923 vw	o
			676 m		677 s	s
668 s	670 s	670 m	670 m	673 m	667 s	s
657 m	661 m	654 m	659 m	650 m	659 m	s
639 m	642 w	643 m	639 w		639 w	t
				621 m	620 m	t
612 s	610 s	615 m	610 m	614 sh	613 m	t
480 m	484 w	481 m	481 w	485 w	485 m	x
466 m	465 m	470 m	467 m	471 m	466 s	x
	364 w			345 w	344 w	v
			336 m	338 m	337 m	u
328 m	328 m	330 m	331 m	331 m	331 m	v
315 m	319 bm	317 m	320 sh	318 m	319 m	v
				316 w	317 w	u
300 m	299 w	299 m	299 w	300 m	299 m	v
	281 vw	282 m	281 w	282 w	282 w	v
273 m	275 w	274 m	274 w	274 m	274 m	v

Figure 25  
Infrared Spectra of Chromic Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

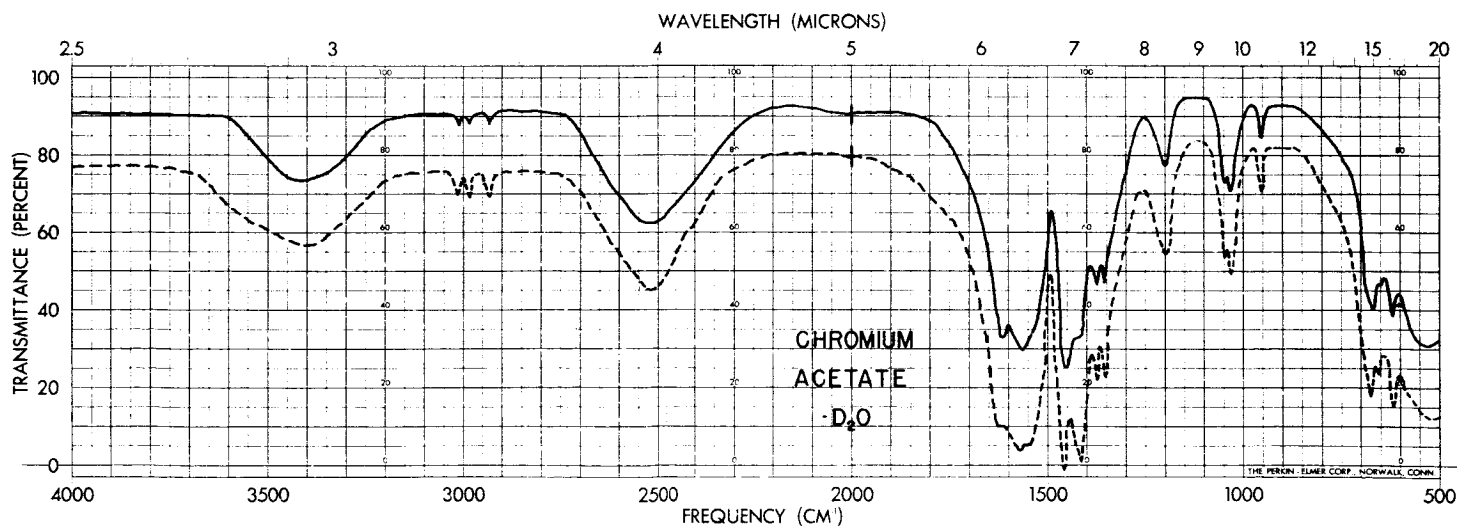
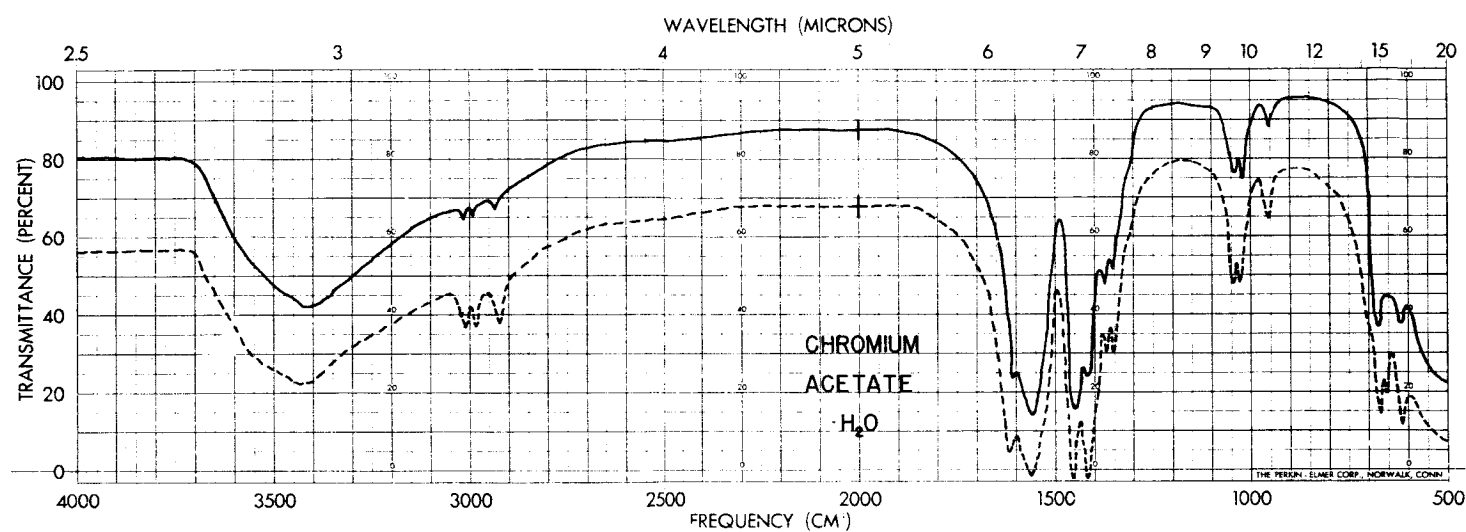
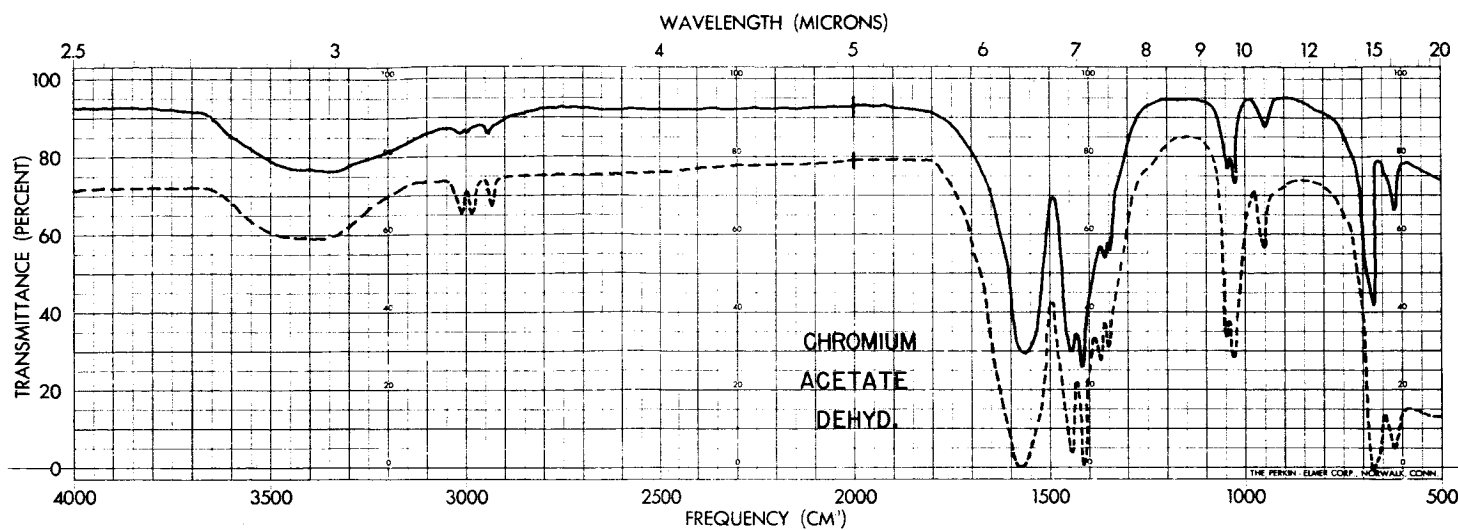




Table XVIII

Infrared Absorption Bands of Chromic Acetate Dehyd.,  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ 

Chromium Acetate Dehyd.		Chromium Acetate $\text{H}_2\text{O}$		Chromium Acetate $\text{D}_2\text{O}$		Assgn.
Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	
		3425 bm	3425 bm			b
3015 vw	3012 vw	3015 vw	3010 vw	3015 vw	3015 vw	c
2999 vw	2985 vw	2990 vw	2985 vw	2985 vw	2985 vw	c
2940 vw	2932 vw	2935 vw	2925 vw	2934 vw	2931 vw	d
				2524 bs	2515 bs	f
		1610 s	1619 s	1615 sh	1625 sh	g
1564 bs	1571 bs	1568 s	1565 s	1566 s	1570 s	h
					1550 sh	h
1445 bs	1442 s	1450 s	1458 s	1451 s	1460 s	i
1418 s	1415 s	1420 s	1419 s	1422 sh	1416 s	j
1360 w	1372 w	1373 w	1371 w	1371 w	1372 w	k
1347 w	1351 w	1354 w	1353 w	1351 w	1354 w	k
				1200 m	1200 m	m
1043 w	1047 w	1041 m	1045 m	1044 m	1047 m	n
1027 m	1030 m	1027 m	1030 m	1031 m	1032 m	n
950 w	952 w	952 w	954 w	952 w	952 w	o
673 s	676 s	673 s	674 s	673 s	668 s	s
			661 m	656 vw	651 vw	s
621 m	620 m	621 s	620 s	620 s	618 m	t
		571 bw	568 bw	561 bw	562 bw	u
		531 bw	532 bw	536 bw	524 bw	u
440 bm	444 bm	440 bm	442 m	440 w	439 w	x
426 vw	425 vw	424 vw	422 w	424 vw	422 vw	x
411 m	410 m	410 m	409 s	408 w	407 w	x
				361 vw	362 vw	u
322 vw						v
315 w	317 w					v
	299 w	296 m	294 m			v
290 m	293 m			292 m	291 m	v
284 w	285 w	284 w	284 w	283 vw	281 w	v
272 m	272 m	273 m	270 m	272 m	272 m	v
				270 m	268 m	u

coordinated water absorptions at  $3270\text{--}3470\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  stretching vibration) and  $1715\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  bending vibration), which shift to  $2408\text{--}2580\text{ cm}^{-1}$  and  $1212\text{ cm}^{-1}$ , respectively, upon exchange of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  as the coordinated water. No coordinated water absorptions were found in the  $700\text{--}900\text{ cm}^{-1}$  region. Coordinated water absorptions were found in the far infrared which are probably due to the librational water modes. The infrared spectra of cupric acetate dehyd.,  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are shown from 2.5 to 20 microns in Figure 26, and complete spectral bands from 2.5 to 40 microns are tabulated in Table XIX.

3. Infrared Spectra of Normal Hydrates, Deuterated Hydrates, and Anhydrous Analogs at Liquid Nitrogen Temperature ( $4000\text{--}250\text{ cm}^{-1}$ ).

a. Calcium acetate. The  $\text{H}_2\text{O}$  stretching vibration in calcium acetate  $\text{H}_2\text{O}$  splits into a doublet ( $3275$  and  $3450\text{ cm}^{-1}$ ) at liquid nitrogen temperature, while the  $\text{D}_2\text{O}$  stretching vibration of calcium acetate  $\text{D}_2\text{O}$  splits into four peaks ( $2348, 2386, 2442$ , and  $2530\text{ cm}^{-1}$ ) at liquid nitrogen temperature. The coordinated water bending vibration sharpens and intensifies at liquid nitrogen temperature. No other well defined coordinated water absorptions are present in the spectrum of calcium acetate  $\text{H}_2\text{O}$ . The infrared spectra of calcium acetate dehyd.,  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines)

Figure 26  
Infrared Spectra of Cupric Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

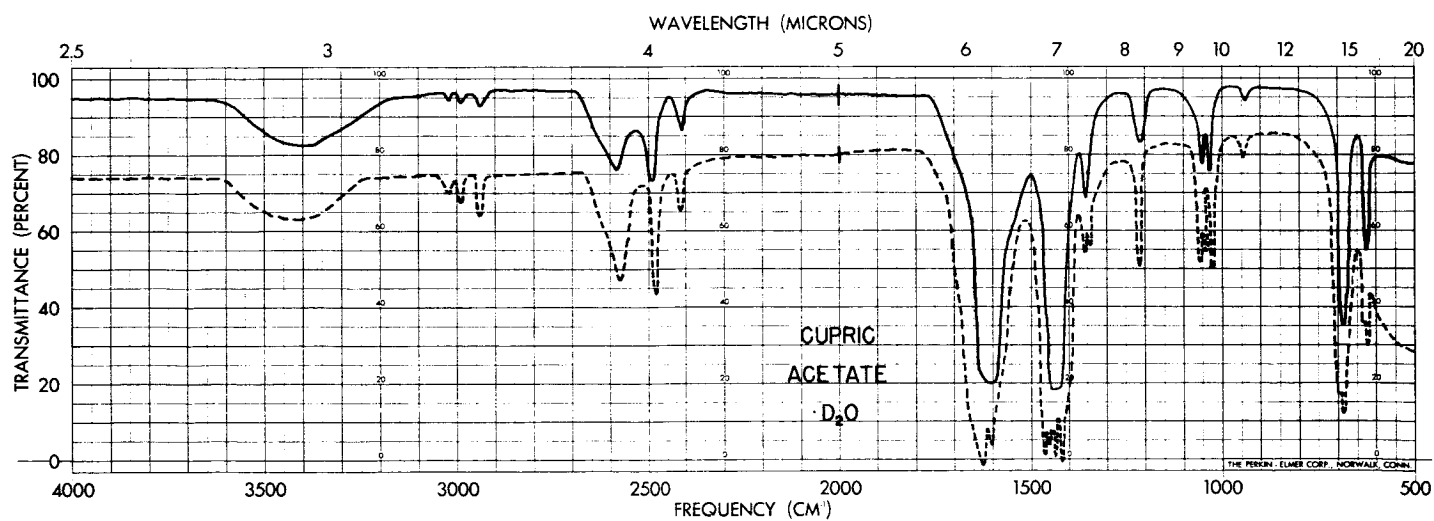
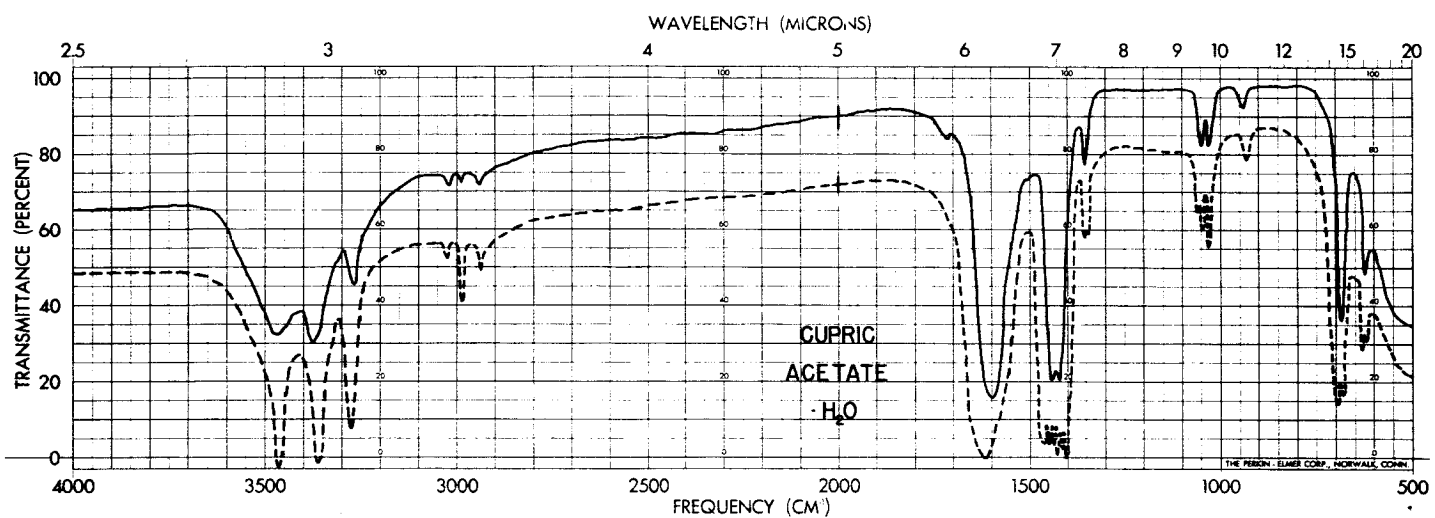
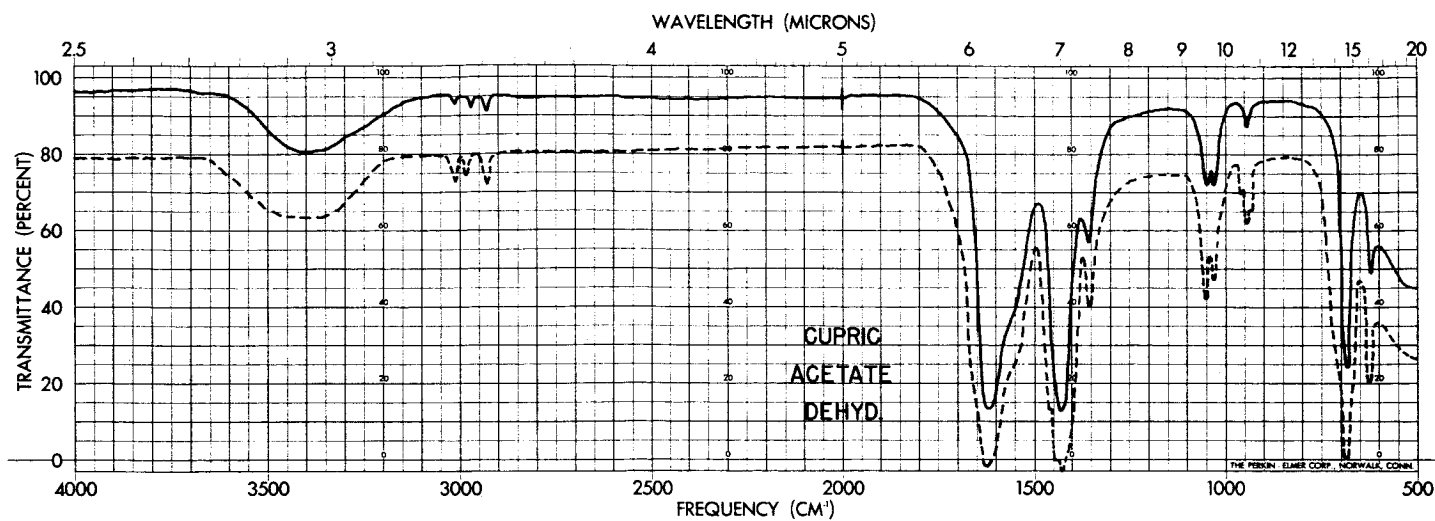


Table XIX

Infrared Absorption Bands of Cupric Acetate Dehyd., .H<sub>2</sub>O and .D<sub>2</sub>O

Cupric Acetate Dehyd.		Cupric Acetate .H <sub>2</sub> O		Cupric Acetate .D <sub>2</sub> O		Assign.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		3470 s	3464 s			b
		3375 s	3360 s			b
		3270 m	3275 s			b
3013 vw	3012 vs	3020 vw	3025 vw	3020 vw	3020 vw	c
2970 vw	2984 vw	2989 vw	2987 w	2990 w	2989 w	c
2930 vw	2928 vw	2940 vw	2938 vw	2940 w	2940 vw	d
				2580 s	2574 s	f
				2490 s	2481 s	f
				2408 m	2415 m	f
		1715 w				g
1620 s	1625 s	1600 s	1615 s	1605 s	1625 s	h
					1607 s	h
	1461 sh		1461 s		1463 s	i
			1455 s		1456 s	i
	1441 sh	1445 s	1446 s		1448 s	i
			1433 s		1439 s	j
1432 s	1428 s	1422 s	1422 s	1430 s	1424 s	j
			1415 s			j
1355 w	1354 w	1353 w	1356 w	1353 w	1358 w	k
			1347 w		1349 w	k
				1212 m	1217 m	m
			1054 w		1056 m	n
1049 w	1050 w	1048 w	1046 w	1050 m	1048 m	n
1034 w	1034 w	1033 w	1032 w	1031 m	1033 m	n
	959 vw					o
	946 w					o
942 w	938 vw	940 vw	935 vw	940 vw	942 vw	o
			693 s		693 sh	s
684 s	686 s	688 s	684 s	687 s	688 s	s
			632 m		634 sh	t
626 m	628 m	626 m	627 m	626 m	629 m	t
			569 w			u
543 bw	546 bw	538 bw	554 w		505 vw	x
			515 w			u
					484 w	u
					425 vw	u
386 s	387 m	377 m		377 w	376 m	v
380 s		372 m	378 s	371 w		v
361 bm	361 m	359 vw				v
341 bm	346 m	342 w		344 vw		v
		337 w	337 m			u
		332 w		333 w	332 w	u
	311 vw		309 vw			v
296 bw	294 bw	299 w	301 w	300 w	300 w	v
		292 w				u
283 w	283 w	284 w	282 w	282 w	282 w	v
274 w	274 w	275 w	275 w	274 w	274 w	v

from 2.5 to 20 microns in Figure 24, while liquid nitrogen temperature spectra of calcium acetate from 2.5 to 40 microns are tabulated in Table XVII.

b. Chromic acetate. The coordinated water absorptions in chromic acetate  $\cdot\text{H}_2\text{O}$  and  $\cdot\text{D}_2\text{O}$  show very little change from room temperature to liquid nitrogen temperature. No apparent shift or splitting of water frequencies appear in hydrated chromic acetate at lowered temperature. The spectra of chromic acetate dehyd.,  $\cdot\text{H}_2\text{O}$  and  $\cdot\text{D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) from 2.5 to 20 microns in Figure 25 while complete spectral bands from 2.5 to 40 microns are tabulated at liquid nitrogen temperature in Table XVIII.

c. Cupric acetate. The  $\text{H}_2\text{O}$  stretching vibration in Cupric Acetate  $\cdot\text{H}_2\text{O}$  shows structure at room temperature, but liquid nitrogen temperature produces a pronounced splitting and intensification of the band into three well defined peaks (3275, 3360, and 3464  $\text{cm}^{-1}$ ) indicative of hydrogen bonded water protons. The  $\text{D}_2\text{O}$  stretching vibration in cupric acetate  $\cdot\text{D}_2\text{O}$  also shows three peaks (2415, 2481, and 2574  $\text{cm}^{-1}$ ) at liquid nitrogen temperature. There are no coordinated water absorptions in the 700-900  $\text{cm}^{-1}$  region and the librational modes in the cesium bromide region are not defined well enough to evidence a definite effect of lowered temperature. The infrared spectra of cupric

acetate dehyd.,  $\text{.H}_2\text{O}$  and  $\text{.D}_2\text{O}$  are shown at liquid nitrogen temperature (broken lines) from 2.5 to 20 microns in Figure 26, while complete spectral bands from 2.5 to 40 microns are tabulated at liquid nitrogen temperature in Table XIX.

#### 4. Acetate Vibrations.

Tables XVII, XVIII, and XIX give acetate assignments for calcium, chromic, and cupric acetates, respectively. It is interesting to note that in cases the acetate fundamentals in these acetates split at liquid nitrogen temperature. This effect was noted occasionally at room temperature. The splitting of the  $1300\text{--}1500\text{ cm}^{-1}$  absorption into the characteristic acetate frequencies was also evident in this series of acetates. Temperature independent acetate vibrations were found in this group of dehydrated, hydrated, and deuterated acetates in the  $250\text{--}300\text{ cm}^{-1}$  segment of the cesium bromide region which are possibly due to a librational motion of the whole molecule within the crystal structure.

#### 5. Discussion of the Bonding.

a. Calcium acetate. As stated, no X-ray data is available on the structure of calcium acetate  $\text{.H}_2\text{O}$  to supplement the infrared analysis. The infrared results alone indicate that there are no free water protons in calcium acetate monohydrate as were found in some of the tetrahydrate acetates. Apparently

all water protons in this hydrate are involved in the formation of hydrogen bonds. From the low temperature splitting of the  $\text{H}_2\text{O}$  stretching absorption into two peaks, and the  $\text{D}_2\text{O}$  stretching absorption into four peaks, hydrogen bonds of different lengths are probably present in the structure. Since no coordinated water absorptions appear in the  $700\text{-}900\text{ cm}^{-1}$  region, there is no infrared evidence for covalent character of the metal-water bonds in calcium acetate  $\cdot\text{H}_2\text{O}$ .

b. Chromic acetate. X-ray data is not available on the structure of chromic acetate  $\cdot\text{H}_2\text{O}$ . Infrared analysis indicates that there are no free water protons present in the structure of chromic acetate  $\cdot\text{H}_2\text{O}$ . The broad  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching absorptions show no splitting at low temperature, thus giving no information as to a difference in hydrogen bond lengths in the structure. There are no coordinated water absorptions in the  $700\text{-}900\text{ cm}^{-1}$  region. There is no infrared evidence for covalent character of the metal-water bonds in this monohydrate.

c. Cupric acetate. X-ray data for cupric acetate  $\cdot\text{H}_2\text{O}$  indicates different hydrogen bond lengths for the protons of the coordinated water molecules. This is substantiated by the infrared analysis which shows definite splitting of the  $\text{H}_2\text{O}$  stretching absorption. The distance between copper atoms



in the structure is 2.64Å, which may indicate a Cu-Cu bond. Unfortunately, if this bond is present, infrared spectroscopy would be of little help in substantiating its presence. Needless to say, no absorption characteristic of a metal-metal interaction was found in the spectrum of cupric acetate  $\cdot\text{H}_2\text{O}$ . There are probably no free water protons present in hydrated cupric acetate; i.e., all water protons are involved in the formation of hydrogen bonds. No coordinated water absorptions are present in the  $700\text{--}900\text{ cm}^{-1}$  region in the hydrate. There is no infrared evidence for covalent character of the metal-water bonds in cupric acetate  $\cdot\text{H}_2\text{O}$ .

#### E. Strontium Acetate $\cdot\frac{1}{2}\text{H}_2\text{O}$

##### 1. Infrared Spectra of the Normal Hydrate, Deuterated Hydrate, and Anhydrous Analog at Room Temperature ( $4000\text{--}250\text{ cm}^{-1}$ ),

Strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$  shows absorption at 3285, 3370, and  $3495\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  stretching vibration), with the  $\text{H}_2\text{O}$  bending vibration being obscured by the asymmetric  $\text{CO}_2$  stretching frequency in the hydrate. The coordinated water stretching vibration shifts to 2405, 2480, and  $2515\text{ cm}^{-1}$  in the deuterated hydrate and disappears from the spectrum of dehydrated strontium acetate. The  $\text{D}_2\text{O}$  bending vibration is very weak at room temperature and occurs at approximately  $1245\text{ cm}^{-1}$  in strontium acetate

$\cdot\frac{1}{2}\text{D}_2\text{O}$  and is absent from the spectrum of the dehydrated complex.

Strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$  has a coordinated water absorption at  $885\text{ cm}^{-1}$ , which shifts upon preparation of the deuterated hydrate, and is absent from the spectrum of dehydrated strontium acetate and is assigned as a rocking, twisting, or wagging vibration of the coordinated water. No coordinated water absorption was found in the cesium bromide region in either the normal or deuterated hydrate. Unfortunately X-ray data is not available on the structure of strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$ . The infrared spectra of strontium acetate are shown from 2.5 to 20 microns in Figure 27, while complete spectral bands from 2.5 to 40 microns are presented with assignments in Table XX.

## 2. Infrared Spectra of the Normal Hydrate, Deuterated Hydrate, and Anhydrous Analog at Liquid Nitrogen Temperature (4000-250 $\text{cm}^{-1}$ )

The  $\text{H}_2\text{O}$  stretching region of strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$  shows three distinct absorptions ( $3275$ ,  $3365$ , and  $3474\text{ cm}^{-1}$ ) at liquid nitrogen temperature while the  $\text{D}_2\text{O}$  stretching region of the deuterated hydrate shows five distinct absorptions ( $2278$ ,  $2399$ ,  $2461$ ,  $2481$ , and  $2515\text{ cm}^{-1}$ ) at liquid nitrogen temperature. The  $\text{H}_2\text{O}$  bending vibration occurs at  $1715\text{ cm}^{-1}$  in the hydrate and shifts to  $1216$ - $1288\text{ cm}^{-1}$  in strontium acetate  $\cdot\frac{1}{2}\text{D}_2\text{O}$  at liquid nitrogen temperature. These absorptions are absent from the

Figure 27  
Infrared Spectra of Strontium Acetate at Room  
Temperature and Liquid Nitrogen Temperature  
in the (4000 - 500  $\text{cm}^{-1}$ ) Region  
\_\_\_\_\_ = Room Temperature  
----- = Liquid Nitrogen Temperature

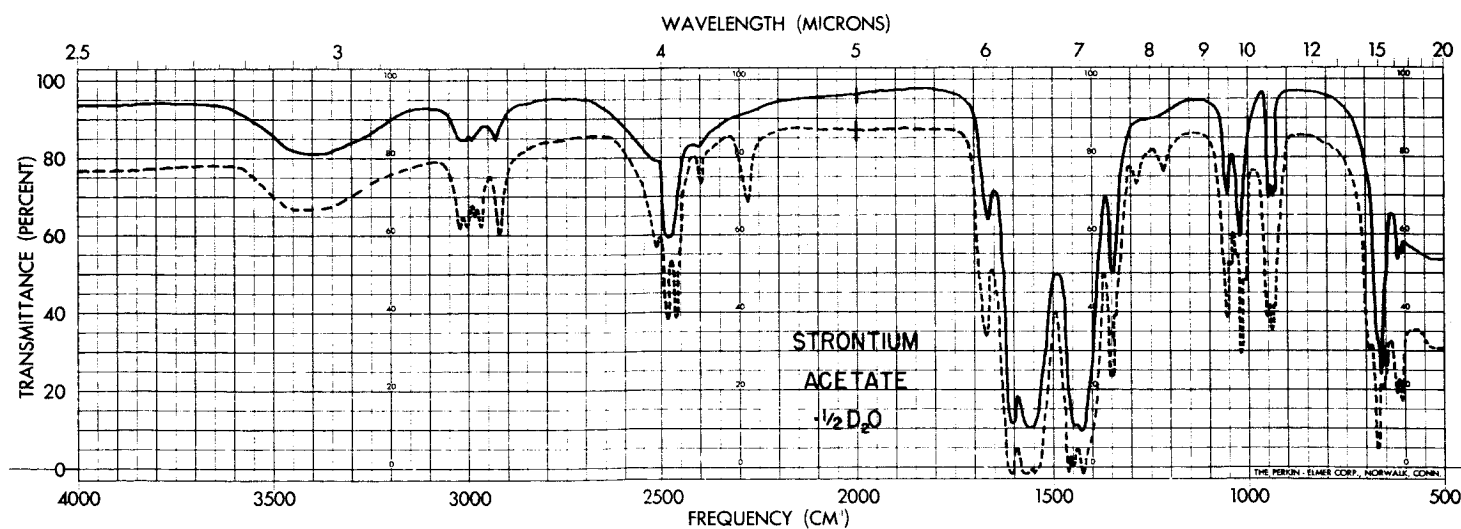
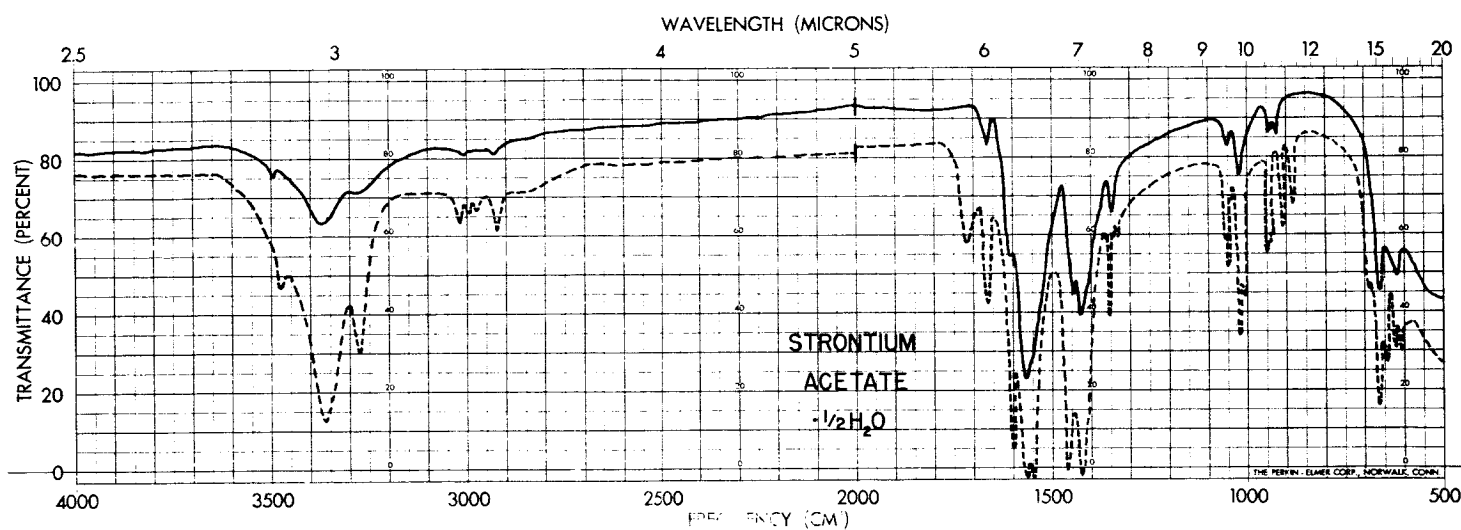
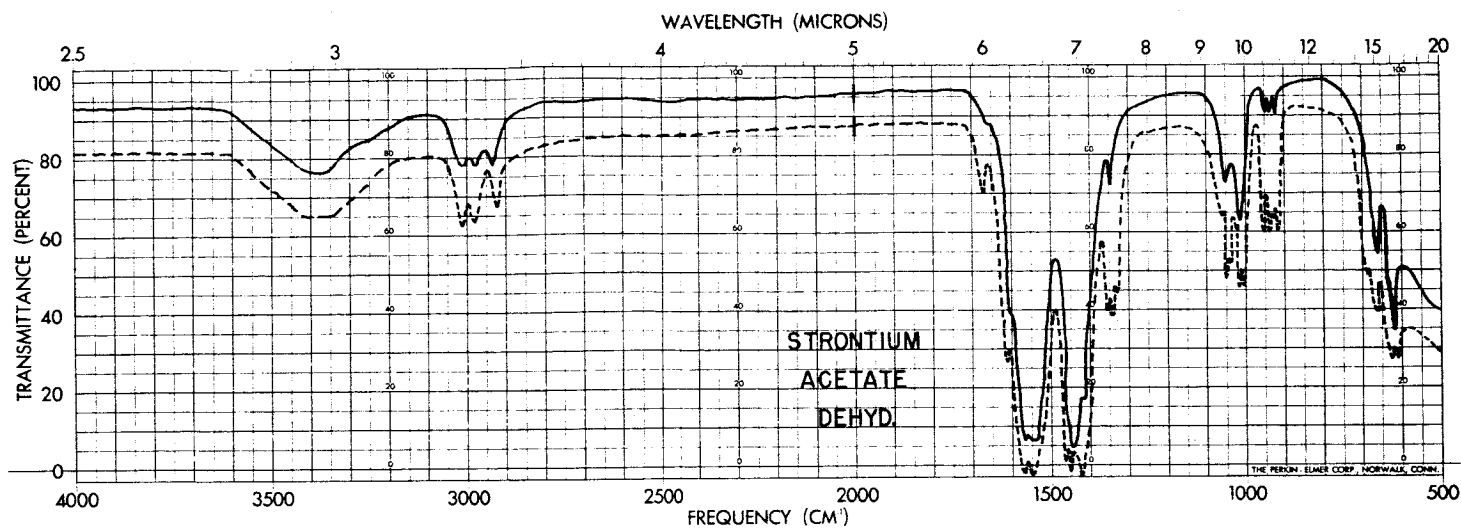


Table XX

Infrared Absorption Bands of Strontium Acetate Dehyd.,  $\frac{1}{2}\text{H}_2\text{O}$  and  $\frac{1}{2}\text{D}_2\text{O}$ 

Strontium Acetate Dehyd		Strontium Acetate. $\frac{1}{2}\text{H}_2\text{O}$		Strontium Acetate. $\frac{1}{2}\text{D}_2\text{O}$		Assn
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
3010 vw	3010 vw	3495 w 3370 s 3285 m 3010 vw	3474 m 3365 s 3275 m 3018 w	3015 vw	3020 w 3005 w	b b b c c
2980 vw	2986 vw 2973 vw		2992 vw 2973 vw	2990 vw	2986 w 2976 w	c c
2931 vw	2923 w	2930 vw	2921 w	2929 vw 2515 m 2480 s 2405 m	2923 w 2515 m 2481 s 2461 s 2399 m 2278 m	d f f f f f
1660 w 1606 s 1568 bs 1549 s	1669 w 1609 s 1566 s 1549 s 1463 s	1715 vw 1660 w 1605 m 1562 bs	1715 w 1664 w 1598 s 1562 s 1549 s 1462 s	1664 w 1605 m 1560 bs	1669 w 1607 s 1564 s 1550 s 1462 s	g h h h i
1440 s 1415 s	1452 s 1424 s	1442 s 1427 s	1426 s 1366 vw 1353 m 1347 w 1343 w	1447 sh 1428 bs	1450 s 1424 s	i j
1345 w	1354 m 1348 m 1343 w	1346 w		1352 w 1348 w	1353 m 1348 m 1343 w 1288 vw 1216 vw	k k k m m
1050 w	1058 vw 1053 m 1046 w 1030 w	1051 w	1057 m 1052 m 1044 w	1051 w	1053 m 1046 w 1030 w	n n n
1020 m	1022 m 1016 m	1020 m	1019 m 1013 m	1020 m	1022 m 1016 w	n n
946 w 939 w 934 w 924 w	951 m 942 m 937 m 924 m	947 w 940 w 934 w 909 w	949 m 942 m 936 m 911 m	948 m 940 m 934 m	950 m 943 m 937 m	o o o o

Table XX (continued)

Infrared Absorption Bands of Strontium Acetate Dehyd.,  $\cdot\frac{1}{2}\text{H}_2\text{O}$  and  $\cdot\frac{1}{2}\text{D}_2\text{O}$ 

Strontium Acetate Dehyd		Strontium Acetate $\cdot\frac{1}{2}\text{H}_2\text{O}$		Strontium Acetate $\cdot\frac{1}{2}\text{D}_2\text{O}$		Assn.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
		885 w	885 m			p
658 s	687 w 660 s	660 s	690 m 666 s	664 s	688 sh 668 s	s
619 m	625 m 611 m	619 m	645 s 623 m 611 m	660 s 619 m 612 m	663 s 623 m 612 m	s
	472 m 468 m		467 m	475 w	472 w	t
463 m	459 m	462 m	459 m	464 m	459 m	x
311 w	308 w	310 w	307 w	310 w	308 w	x
299 w	298 m	298 w	299 m	299 w	299 w	v
			292 vw			v
282 w	282 m	282 w	282 m	284 w	281 w	v
273 w	273 m	273 w	274 m	274 w	274 w	v

spectrum of dehydrated strontium acetate. The rocking, twisting, or wagging vibration occurs at  $885\text{ cm}^{-1}$  in the hydrate with intensification at liquid nitrogen temperature. No coordinated water absorptions are found in the far infrared at low temperature. The spectra of strontium acetate are shown from 2.5 to 20 microns at liquid nitrogen temperature (broken lines) in Figure 27, and complete liquid nitrogen spectra from 2.5 to 40 microns are presented with assignments in Table XX.

### 3. Acetate Vibrations.

Table XX lists acetate assignments for strontium acetate dehyd.,  $\cdot\frac{1}{2}\text{H}_2\text{O}$  and  $\cdot\frac{1}{2}\text{D}_2\text{O}$ . It is interesting to observe the effect of liquid nitrogen temperature upon the acetate frequencies of strontium acetate. Most of the acetate frequencies split into doublets or triplets at lowered temperature in this complex under high resolution. This effect is not caused by the KBr matrix since the low temperature splittings were duplicated by examining both mull and powder film spectra at liquid nitrogen temperature. It is interesting to observe the effect of low temperature on the acetate vibrations in the  $1300\text{--}1500\text{ cm}^{-1}$  region. From analysis of the other acetate complexes and from assignments of frequencies for sodium acetate by other workers, we expect four fundamentals in this region. At liquid nitrogen temperature, however, as many as six distinct peaks are observed

in this region. Acetate vibrations in the low energy segment of the cesium bromide region from  $270\text{--}311\text{ cm.}^{-1}$  are observed. These absorptions were found in all the acetates studied and are tentatively assigned to a librational motion of the whole molecule in the crystal structure.

#### 4. Discussion of the Bonding.

Since X-ray or other structural data are not available for strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$ , infrared spectral data can give only an indication of the bonding present in the crystal structure. Apparently no free water protons are present in the structure of strontium acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$ ; i.e., all water protons are involved in hydrogen bonding. Since the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching vibrations show definite splittings at both room temperature and especially at liquid nitrogen temperature, hydrogen bonds of different strengths are probably present in the structure of this hydrate. Since a coordinated water absorption appears which is assigned as a wagging, twisting, or rocking mode, there is probably some covalent character attached to the metal-water bonds in this hydrate.

#### F. Basic Aluminum and Basic Thorium Acetates $\cdot\text{H}_2\text{O}$ .

##### 1. Infrared Spectra of Basic Hydrates at Room Temperature and Liquid Nitrogen Temperature ( $4000\text{--}250\text{ cm.}^{-1}$ ).

a. Basic aluminum acetate  $\cdot\text{H}_2\text{O}$ . This hydrate,



which has the formula  $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , gives rise to a sharp absorption at  $3703 \text{ cm}^{-1}$  (free O-H stretching vibration) at room temperature which intensifies and shifts slightly to  $3711 \text{ cm}^{-1}$  at liquid nitrogen temperature. A broad absorption due to the coordinated water stretching vibration appears at  $3450 \text{ cm}^{-1}$  at room temperature and retains its form but shifts to approximately  $3425 \text{ cm}^{-1}$  at liquid nitrogen temperature. No structure appears in this band at either room temperature or at liquid nitrogen temperature. The  $\text{H}_2\text{O}$  bending vibration occurs at  $1711 \text{ cm}^{-1}$  and  $1710 \text{ cm}^{-1}$  at room temperature and at liquid nitrogen temperature, respectively. No coordinated water absorptions appear in the  $700\text{-}900 \text{ cm}^{-1}$  region. An absorption is present at  $506\text{-}511 \text{ cm}^{-1}$  in the cesium bromide region which is tentatively assigned to a librational water mode. This hydrate could not be dehydrated successfully since apparently the coordinated water is held so tightly that the acetate decomposes before dehydration is effected.  $\text{D}_2\text{O}$  could not be exchanged for  $\text{H}_2\text{O}$  in good yield in the crystal lattice of this hydrate. Hence only the normal hydrate has been studied. The infrared spectra of basic aluminum acetate hydrate is shown from 2.5 to 20 microns at both room and liquid nitrogen temperatures in Figure 28-A, while complete spectral bands are tabulated from 2.5 to 40 microns at room temperature and at liquid nitrogen temperature in Table XXI. X-ray data is not available concerning the structure of

basic aluminum acetate  $\cdot\text{H}_2\text{O}$ .

b. Basic thorium acetate  $\cdot\text{H}_2\text{O}$ . Basic thorium acetate hydrate,  $\text{Th}(\text{OH})_2(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , gives rise to a sharp absorption at  $3650\text{ cm}^{-1}$  at room temperature, shifting to  $3652\text{ cm}^{-1}$  at liquid nitrogen temperature (free O-H stretching vibration). The  $\text{H}_2\text{O}$  bending vibration is not distinct at room temperature but appears at  $1655\text{ cm}^{-1}$  at liquid nitrogen temperature. No coordinated water absorptions appear in the  $700\text{--}900\text{ cm}^{-1}$  region in this hydrate. Absorptions at  $370\text{--}487\text{ cm}^{-1}$  in the cesium bromide region are tentatively assigned to librational modes of the coordinated water. As with the basic aluminum hydrate, attempts to dehydrate basic thorium acetate  $\cdot\text{H}_2\text{O}$  were unsuccessful apparently because decomposition occurred before the coordinated water was removed. A similar low yield of the deuterated hydrate was evidenced. Thus only the normal hydrate has been studied here. The infrared spectra of basic thorium acetate  $\cdot\text{H}_2\text{O}$  is shown from 2.5 to 20 microns at both room temperature and liquid nitrogen temperature in Figure 28-B, while complete spectral bands are tabulated from 2.5 to 40 microns at room temperature and at liquid nitrogen temperature in Table XXI. X-ray data is not available for basic thorium acetate  $\cdot\text{H}_2\text{O}$ .

Figure 28  
Infrared Spectra of Basic Aluminum and  
and Basic Thorium Acetates  $\cdot\text{H}_2\text{O}$   
and Anhydrous Barium Acetate in the  
(4000 - 500  $\text{cm}^{-1}$ ) Region

\_\_\_\_\_ = Room Temperature

----- = Liquid Nitrogen Temperature

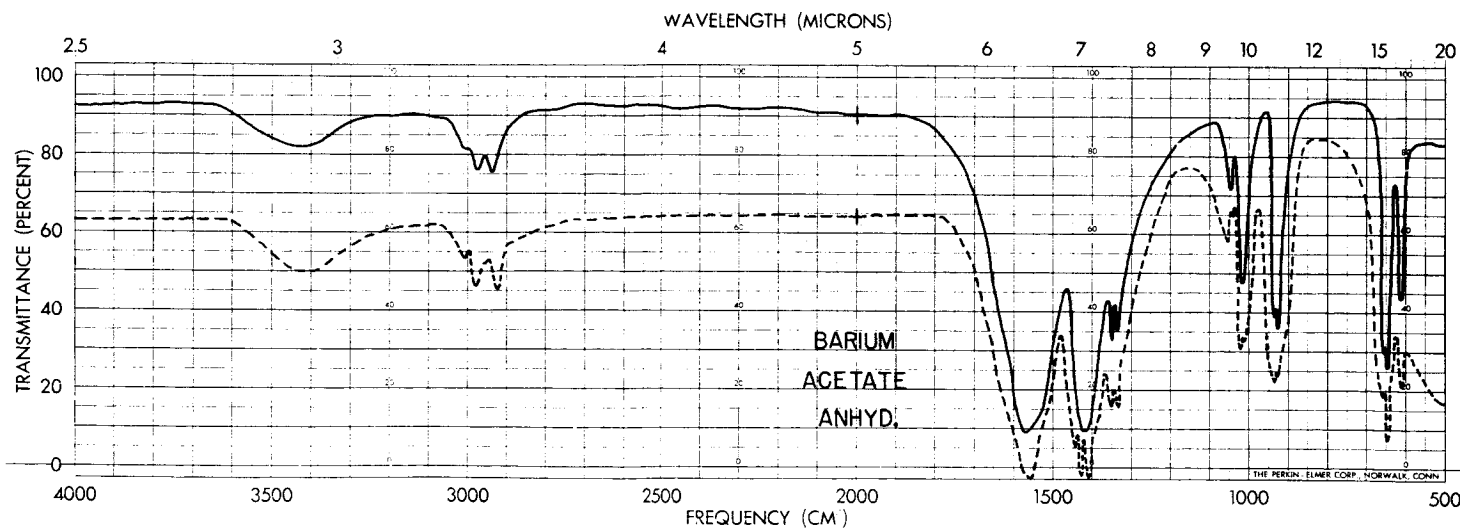
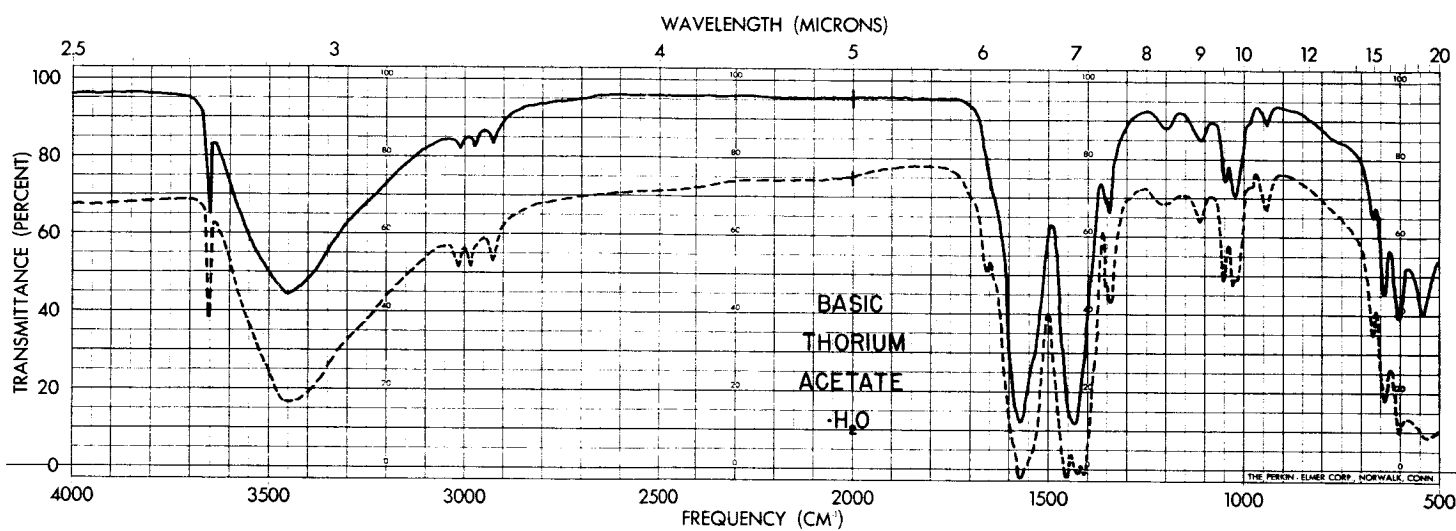
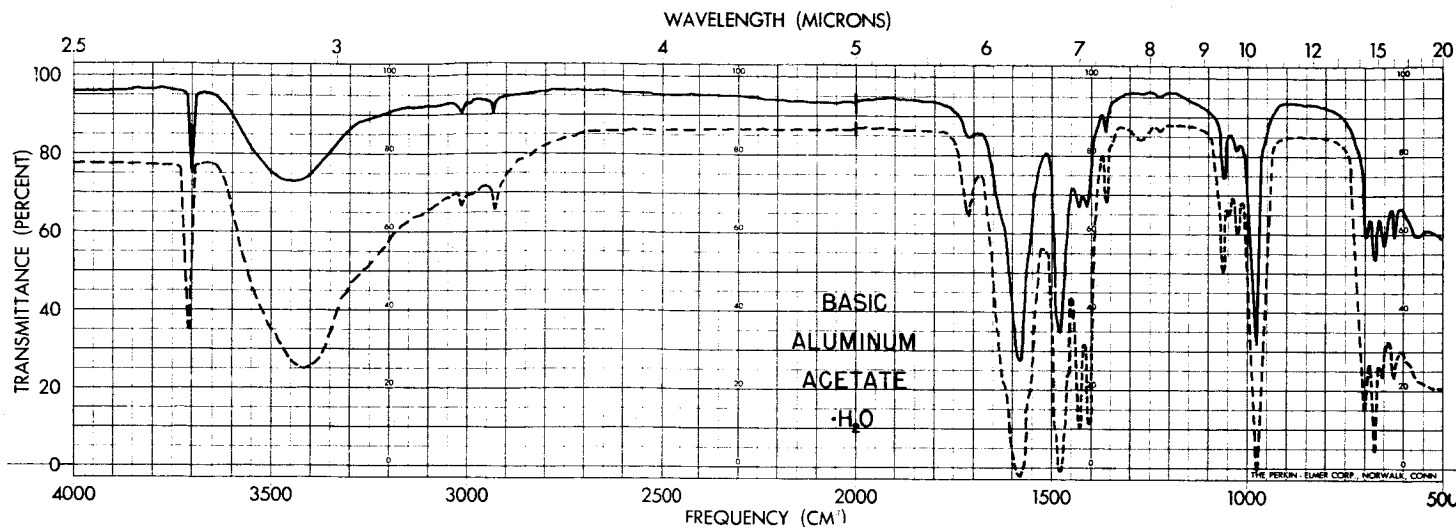


Table XXI

Infrared Absorption Bands of Basic Aluminum  
and Basic Thorium Acetates  $\cdot\text{H}_2\text{O}$ 

Basic Aluminum Acetate $\text{Al}(\text{OH})(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$		Basic Thorium Acetate $\text{Th}(\text{OH})_2(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$		Assign.
Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	Room Temp $\text{Cm}^{-1}$ I	Liq. $\text{N}_2$ Temp $\text{Cm}^{-1}$ I	
3703 m	3711 m	3650 m	3652 m	z
3450 bm	3425 bm	3450 bm	3450 bm	b
3015 vw	3015 vw	3010 vw	3012 vw	c
2995 vw	2990 vw	2975 vw	2982 vw	c
2933 vw	2930 vw	2926 vw	2927 vw	d
1711 w	1710 w		1655 w	g
1582 s	1580 s	1572 s	1573 s	h
1478 s	1478 s		1452 s	i
1431 m	1428 s	1434 s	1425 s	j
1411 m	1406 m		1415 s	i
1362 w	1362 w	1350 m	1353 m	k
		1341 m	1340 m	k
		1110 w	1116 m	m
1060 m	1063 m	1047 m	1051 m	n
	1051 w		1031 m	n
1028 m	1029 m	1022 m	1025 vw	n
978 s	974 s	990 vw	993 vw	o
		940 w	941 w	o
696 m	701 s			s
677 s	678 s	668 w	670 w	s
651 m	658 m	640 m	639 s	t
623 m	626 m	603 s	603 m	t
568 bm	573 m	547 s	549 s	x
506 bm	511 bm	487 vw	487 w	u
		400 vw	400 vw	u
		377 m	374 bm	u
		370 m	370 m	u
345 m	347 m			v
310 w	309 w	312 vw		v
297 bm	299 bm	295 w	295 w	v
289 w	291 m			v
281 w	281 w	284 vw	283 w	v
272 bm	272 bm	271 w	270 w	v

## 2. Acetate Vibrations.

Acetate vibrations for basic aluminum acetate  $\cdot\text{H}_2\text{O}$  and basic thorium acetate  $\cdot\text{H}_2\text{O}$  are tabulated with assignments at both room temperature and at liquid nitrogen temperature from 2.5 to 40 microns in Table XXI. The  $1300\text{--}1500\text{ cm}^{-1}$  region again splits into the characteristic acetate frequencies at liquid nitrogen temperature. Acetate vibrations were found in the low energy segment of the cesium bromide region at  $270\text{--}312\text{ cm}^{-1}$ . These absorptions are not affected by low temperature and are tentatively assigned to a librational motion of the whole molecule within the crystal structure. The remaining acetate frequencies are similar to those found and discussed previously and are essentially standard from acetate to acetate except for the strong absorption at  $978\text{ cm}^{-1}$  in basic aluminum acetate which is probably due to the Al-O-Al bond. The Al-O-Al absorption overlaps the C-C stretch in basic aluminum acetate.

## 3. Discussion of the Bonding.

X-ray diffraction data is not available concerning the structure of either basic aluminum or basic thorium hydrated acetates. Infrared analysis indicates a sharp absorption at  $3650\text{--}3711\text{ cm}^{-1}$  in these complexes which is assigned as the free O-H stretching vibration. This absorption occurs at a higher frequency and is sharper than the free water proton

absorption that was found in some of the tetrahydrate acetates. The hydrogen bonded stretching absorption in basic aluminum and basic thorium acetates  $\cdot\text{H}_2\text{O}$  shows no structure at liquid nitrogen temperature and indicates that all of the protons of the coordinated water molecules are involved in hydrogen bonding. Coordinated water absorptions do not occur in the  $700\text{-}900\text{ cm}^{-1}$  region. No absorption characteristic of a metal-oxygen bond was found. There is no infrared evidence for covalent character of the metal-water bonds in basic aluminum and basic thorium hydrated acetates.

#### G. Anhydrous Acetates

The following anhydrous acetates were studied: barium mercuric, potassium, silver, and thallous acetates. The infrared spectra of these acetates had not been studied before, and no absorption band assignments had been made. It was of interest to assign acetate vibrations in these anhydrous complexes as an aid in determining a range for these vibrations in general so that coordinated water absorptions in the hydrated acetates could be distinguished.

##### 1. Infrared Spectra of Anhydrous Acetates at Room Temperature and Liquid Nitrogen Temperature ( $4000\text{-}250\text{ cm}^{-1}$ )

A great similarity in acetate vibrational frequencies is found in progressing from acetate to acetate as would be

expected. The infrared spectra from 2.5 to 20 microns of barium acetate,  $(\text{CH}_3\text{COO})_2\text{Ba}$ , mercuric acetate  $(\text{CH}_3\text{COO})_2\text{Hg}$ , potassium acetate,  $\text{CH}_3\text{COOK}$ , silver acetate,  $\text{CH}_3\text{COOAg}$ , and thallous acetate,  $\text{CH}_3\text{COOTl}$  are shown in Figures 28-C, 29-A, 29-B, 29-C, and 16-A, respectively, at room temperature and at liquid nitrogen temperature. Complete spectral band assignments from 2.5 to 40 microns for the anhydrous acetates of barium, mercuric, and potassium are tabulated in Table XXII, while this data for anhydrous silver and thallous acetates are presented in Table XXIII.

The acetate frequencies are given with assignments and the Tables should be self-explanatory if used in conjunction with the key to absorption band assignments (Table V). It is again interesting to note the 1300-1500  $\text{cm}^{-1}$  region in the anhydrous acetates because it generally shows an excellent splitting into the characteristic acetate peaks at liquid nitrogen temperature which are usually unresolved at room temperature. The effect of liquid nitrogen temperature is generally to sharpen and intensify any given acetate fundamental. The low energy segment of the cesium bromide region from approximately 250-350  $\text{cm}^{-1}$  shows acetate absorptions similar to those found in the precedingly discussed acetate complexes, which are tentatively assigned to a librational motion of the whole molecule within the crystal structure.



Figure 29  
Infrared Spectra of Mercuric, Potassium,  
and Silver Anhydrous Acetates at Room  
Temperature and Liquid Nitrogen Temperature  
(4000 - 500  $\text{cm}^{-1}$ )

\_\_\_\_\_ = Room Temperature

----- = Liquid Nitrogen Temperature

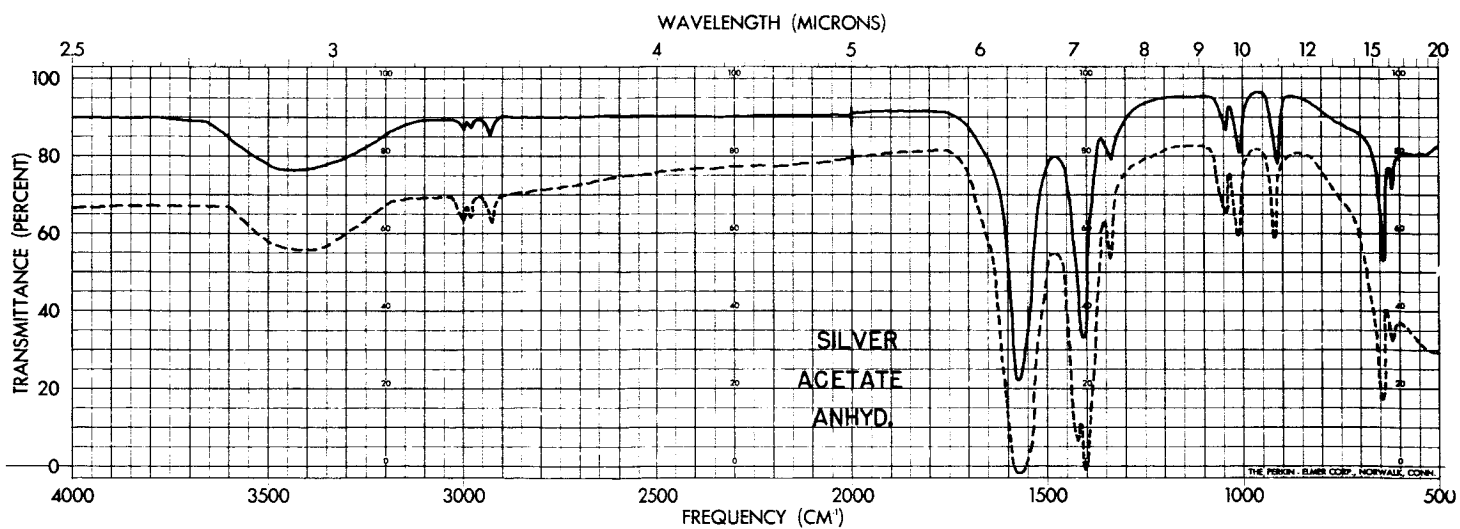
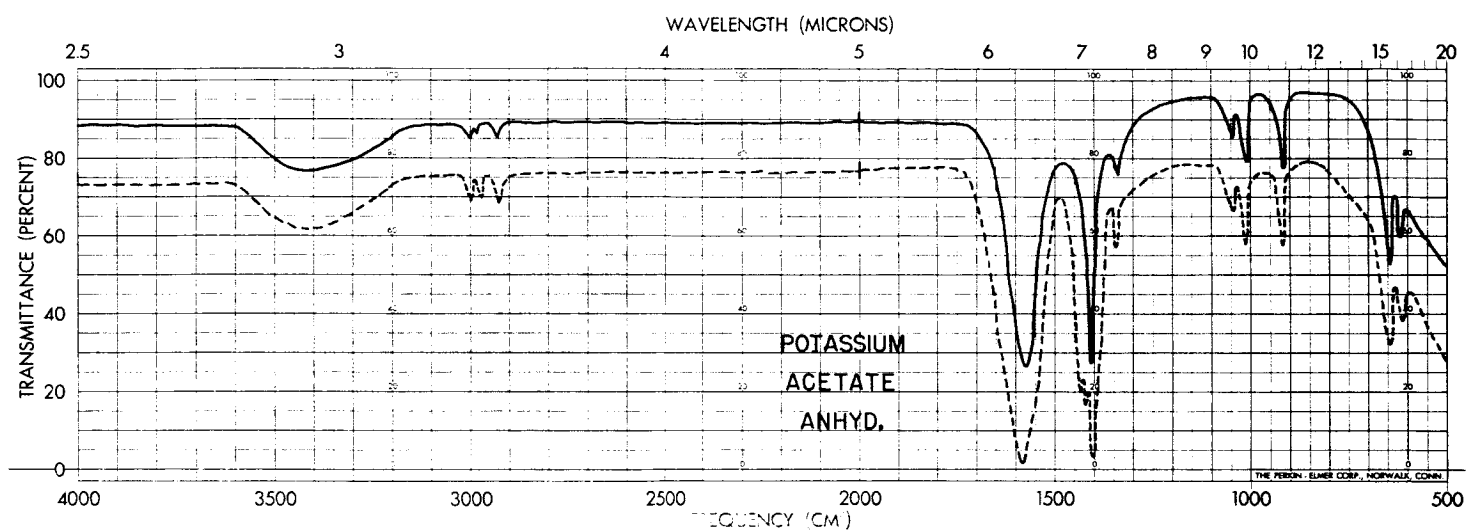
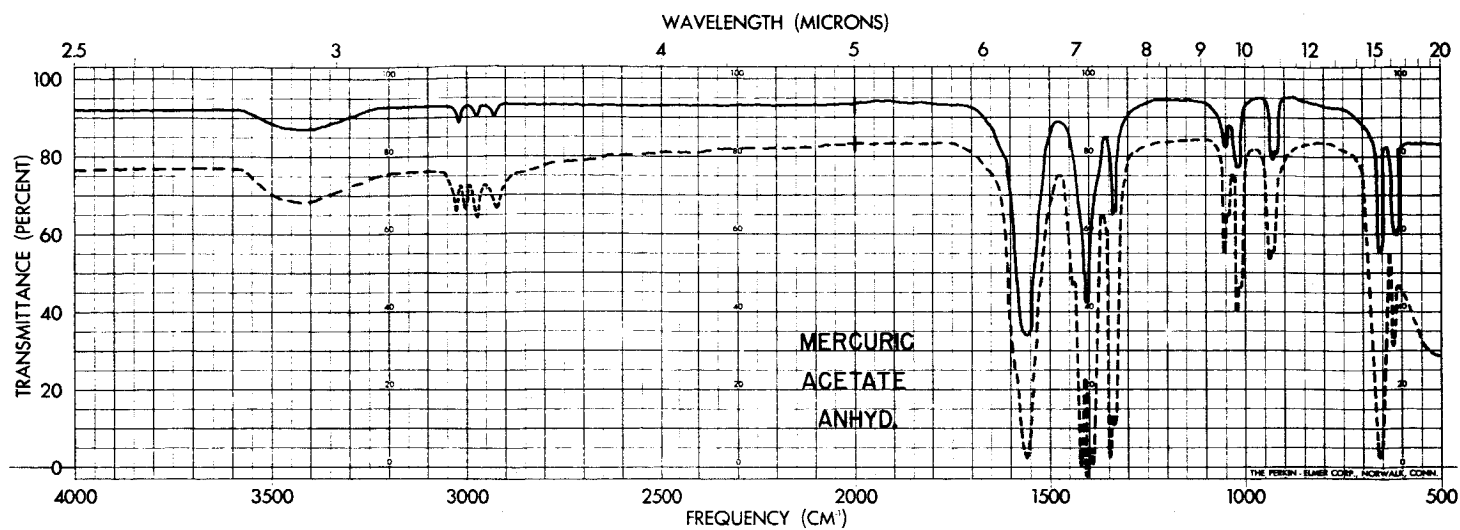


Table XXII

Infrared Absorption Bands of Barium,  
Mercuric, and Potassium Anhydrous Acetates

Barium Acetate Anhyd		Mercuric Acetate Anhyd		Potassium Acetate Anhyd		Assn
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
3010 vw	3008 vw	3020 w	3026 w 3004 vw	3000 vw	2998 vw	c
2975 vw	2978 vw	2975 w	2976 vw	2983 vw	2972 vw	c
2936 vw	2921 w	2930 w	2924 vw	2930 vw	2926 vw	c
		1618 s				d
		1602 s				h
1568 bs	1555 s	1570 s	1560 s	1575 bs	1582 s	h
	1442 w		1440 sh		1439 w	i
	1426 s		1421 s		1423 w	i
1417 bs	1408 s	1403 s	1406 s	1410 s	1403 s	j
			1397 s			j
1348 w	1350 w	1344 m	1347 m			k
1338 w	1336 w	1338 m	1339 m	1338 w	1345 w	k
	1051 w		1054 m			n
1046 w	1039 vw	1048 w	1048 w	1044 w	1042 w	n
	1020 m		1023 w			n
1016 m	1012 m	1018 w	1020 m	1008 m	1015 m	n
933 w	935 m	932 m	936 w			o
929 m	929 m	924 w	931 w	918 m	919 m	o
653 m	655 m	655 s	658 s	643 s	644 s	s
649 s	649 s					s
614 m	614 m	615 m	624 m	619 m	615 s	t
	466 m	467 m	473 m			x
461 m	459 m		465 m	456 m	456 m	x
310 w	309 w	309 w	309 w	309 w	309 w	v
297 w	298 w	297 w	298 w	299 w	297 w	v
292 vw	291 vw					v
282 w	282 m	281 w	283 w	282 w	281 w	v
272 w	273 w	273 w	273 w	273 w	273 w	v

Table XXIIIInfrared Absorption Bands of Silver  
and Thallous Anhydrous Acetates

Silver Acetate Anhyd		Thallous Acetate Anhyd		Assgn.
Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	Room Temp Cm. <sup>-1</sup> I	Liq. N <sub>2</sub> Temp Cm. <sup>-1</sup> I	
2999 vw	3000 vw	3015 vw	2998 vw	c
2980 vw	2980 vw	2972 vw	2977 vw	c
2930 vw	2928 vw	2930 vw	2924 vw	d
		1720 w		
1575 s	1570 s	1575 s	1577 s	h
	1422 s		1424 sh	i
1410 s	1403 s	1404 s	1404 s	j
			1343 w	k
1336 w	1339 w	1335 w	1338 w	k
1042 w	1043 w	1043 w	1045 w	n
1008 m	1014 m	1011 w	1018 w	n
	920 m	919 m	921 w	o
912 m		913 m		o
			676 vw	s
642 s	646 s	644 s	649 s	s
620 m	620 m	621 m	620 m	t
457 w	456 m	459 m	462 m	x
310 w	309 vw	310 w	311 vw	v
298 w	299 w	299 w	300 m	v
283 w	279 w	280 w	282 m	v
274 w	274 w	272 w	274 m	v

## 2. Discussion of the Bonding.

Unfortunately X-ray data is not available concerning the structures of these anhydrous acetates. Since there are no coordinated water molecules present, their absorptions cannot be followed to give an indication as to the nature of the bonding present. However, no absorption band was found in the anhydrous acetates in either the sodium chloride or cesium bromide regions which could be assigned to a metal-oxygen vibration. Infrared analysis shows that the spectra of the anhydrous acetates are very similar and that there is no evidence for covalent character of the ligands bonded to the metals in these complexes.

### H. Proton NMR Spectra

Proton NMR spectra were obtained in order to determine the number of coordinated water molecules per molecule of acetate. This was done by integrating the  $\text{CH}_3$  and  $\text{H}_2\text{O}$  peaks and comparing the number of water molecules present per  $\text{CH}_3$  group of the acetate. The acetate complexes were observed at room temperature as weight per cent solutions in 99.7%  $\text{D}_2\text{O}$  using capillary tetramethylsilane as the reference standard. Some of the acetate complexes studied using infrared techniques contain paramagnetic metal ions and are not applicable, as such, to proton NMR analysis. Solubilities of some acetate

salts in  $D_2O$  were not large enough to allow observation of the  $CH_3$  and  $H_2O$  peaks above the noise level. Proton NMR spectra of the acetates which have sufficient solubility in  $D_2O$  and which did not contain paramagnetic metals are presented in Table XXIV. The ratio of  $H_2O/CH_3$  found is presented and compared with the theoretical values. Peak positions are given in p.p.m. and anhydrous acetates are given for comparison purposes. Proton nuclear magnetic resonance was also used in the course of this work to determine the purity of the deuterated hydrates.

Table XXIV

## Proton NMR Data for the Acetate Complexes

Acetate Complex	$\delta_{\text{CH}_3}$ p.p.m.	$\delta_{\text{H}_2\text{O}}$ p.p.m.	$\text{H}_2\text{O}/\text{CH}_3$		% by Weight
			Found	Theoretical	
$\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	2.42	5.49	2:1	2:1	25
$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	2.70	5.53	3:2	3:2	25
$\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$	2.40	5.20	3:1	3:1	20
$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	2.85	5.73	1:1	1:1	25
$\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$	2.70	5.70	2:1	2:1	20
$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	2.54	5.50	1:1	1:1	20
$\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	2.73	5.72	1:2	1:2	30
$\text{Sr}(\text{CH}_3\text{COO})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	2.47	5.37	1:4	1:4	20
$\text{Ba}(\text{CH}_3\text{COO})_2$	2.48	--	---	---	36
$\text{Hg}(\text{CH}_3\text{COO})_2$	2.93	--	---	---	20
$\text{K}(\text{CH}_3\text{COO})$	2.38	--	---	---	20
$\text{Na}(\text{CH}_3\text{COO})$	2.40	--	---	---	20
$\text{Tl}(\text{CH}_3\text{COO})$	2.42	--	---	---	20

## PART IV

## CONCLUSIONS

A. Coordinated Water Absorptions

The position of the coordinated water absorptions in the hydrated metallic acetate complexes is important because it can give an indication as to the nature of the bonding present. If coordinated water absorptions appear only in the  $H_2O$  stretching and bending regions, and if no metal-oxygen band is found, then ionic bonding of ligand to metal is indicated. If, on the other hand, coordinated water absorptions appear not only in the  $H_2O$  stretching and bending regions, but also in the  $700-900\text{ cm}^{-1}$  region, a lowering of the symmetry is indicated, and some covalent character is present in the metal-water bonds. Free water protons have been shown to occur in some of the tetrahydrate acetates, while the remainder of the hydrated acetates show completely hydrogen bonded water protons present. Of the tetrahydrate acetates studied, nickel, cobalt and magnesium tetrahydrate acetates were found to contain free water protons. In these three hydrates, the coordinated water absorptions at  $724-745\text{ cm}^{-1}$  and  $803-813\text{ cm}^{-1}$  appear to be associated with the water molecules containing the free water protons, while the  $H_2O$  absorption, at  $856-904\text{ cm}^{-1}$ , is apparently due to



the remaining water molecules which contain only hydrogen bonded water protons. The remaining hydrates, which do not contain free water protons, do not show more than one water absorption in the  $700\text{--}900\text{ cm}^{-1}$  region.

In many of the hydrated acetates water absorptions are present in the cesium bromide region which show some sensitivity to temperature. These water absorptions have been assigned to a librational motion of the coordinated water molecules. Intra- and inter- molecular hydrogen bonding occurs in some of the hydrated metallic acetates.

A strict correlation between the number of coordinated water molecules present in the various acetates and the number of water absorptions appearing in the infrared spectra does not exist. Table XXV summarizes the coordinated water absorptions found in the 2.5 to 20 micron region at room temperature in the hydrated acetates studied.

#### B. Acetate Vibrations

Acetate vibrations have been found to be reasonably standard in the metallic acetates studied. In some cases acetate frequencies have split into doublets or triplets at lowered temperature. Especially interesting is the  $1300\text{--}1500\text{ cm}^{-1}$  region which shows a broad absorption at room temperature, but splits into the characteristic acetate absorptions at

Table XXV

Characteristic Coordinated Water Absorptions of the  
Hydrated Acetates at Room Temperature in the 2.5 to 20 Micron Region

Hydrated Acetate	Free -OH Stretch- ing $\text{Cm}^{-1}$ I	Free H <sub>2</sub> O Stretch- ing $\text{Cm}^{-1}$ I	Hydrogen Bonded H <sub>2</sub> O Stretching $\text{Cm}^{-1}$ I	H <sub>2</sub> O Bending $\text{Cm}^{-1}$ I	H <sub>2</sub> O Rocking, Twisting, or Wagging $\text{Cm}^{-1}$ I
Cobalt Acetate $\cdot 4\text{H}_2\text{O}$		3492 s	3150 bs	1700 w	880 m, 804 m, 736 m
Magnesium Acetate $\cdot 4\text{H}_2\text{O}$		3527 s	3180 bs	1708 w	856 m, 803 m, 724 m
Manganese Acetate $\cdot 4\text{H}_2\text{O}$			3275 bs, 3388 bs	1706 m	882 w, 760 m
Nickel Acetate $\cdot 4\text{H}_2\text{O}$		3475 s	3150 bs	1690 w	904 m, 813 m, 745 m
Lead Acetate $\cdot 3\text{H}_2\text{O}$			3400 bm	1660 w	
Sodium Acetate $\cdot 3\text{H}_2\text{O}$			3175 s, 3285 s, 3430 bs	$\left\{ \begin{array}{l} 1635 \text{ s} \\ 1695 \text{ m} \end{array} \right\}$ -----	795 bm
Cadmium Acetate $\cdot 2\text{H}_2\text{O}$			3450 bm		
Lithium Acetate $\cdot 2\text{H}_2\text{O}$			3170 bs, 3400 bs	1710 w	858 w
Zinc Acetate $\cdot 2\text{H}_2\text{O}$			3125 bs, 3385 bm	1710 vw	835 w
Calcium Acetate $\cdot \text{H}_2\text{O}$			3400 bm	1605 vw	
Chromic Acetate $\cdot \text{H}_2\text{O}$			3425 bm	1610 s	
Cupric Acetate $\cdot \text{H}_2\text{O}$			3270 m, 3375 s, 3470 s	1715 w	
Strontium Acetate $\cdot \frac{1}{2}\text{H}_2\text{O}$ Basic			3285 m, 3370 s, 3495 w	1715 vw	885 w
Aluminum Acetate $\cdot \text{H}_2\text{O}$ Basic	3703 m		3450 bm	1711 w	
Thorium Acetate $\cdot \text{H}_2\text{O}$	3650 m		3450 bm	-----	-132

lowered temperature. Generally four acetate absorptions in the range  $268\text{--}275\text{ cm.}^{-1}$ ,  $276\text{--}286\text{ cm.}^{-1}$ ,  $287\text{--}303\text{ cm.}^{-1}$  and  $304\text{--}322\text{ cm.}^{-1}$  have been found in every acetate complex studied in the low energy segment of the cesium bromide region. These absorptions have been tentatively assigned to a librational motion of the whole molecule within the crystal structure.

Since the acetate vibrations do not shift a great deal when the cation is changed and are not greatly affected by hydration, it is possible to specify group vibrations for the acetate group. Table XXVI summarizes group vibrations for the acetate group at room temperature from 2.5 to 20 microns in the twenty acetate complexes studied.

### C. Effect of Liquid Nitrogen Temperature

It has been shown that by observing the solid state spectra of the acetates at liquid nitrogen temperature, a great deal of useful information is obtained. Generally all absorption bands sharpen and intensify upon progressing from room temperature to liquid nitrogen temperature. The low temperature technique has been used to show excellent splittings of the broad hydrogen bonded  $\text{H}_2\text{O}$  stretching absorption into peaks characteristic of the type of hydrogen bonded water present. By using a high resolution grating spectrophotometer and by observing the spectra of the acetates at liquid nitrogen

Table XXVI

Acetate Group Vibrations at  
Room Temperature in the 2.5 to 20 Micron Region

<u>Acetate Vibration</u>	<u>Range (Cm.<sup>-1</sup>)</u>	<u>Intensity</u>
CH <sub>3</sub> asymmetrical stretching	2970-2999, 2999-3020	vw-w
CH <sub>3</sub> symmetrical stretching	2925-2940	vw-w
CO <sub>2</sub> asymmetrical stretching	1514-1665	s-vs
CH <sub>3</sub> asymmetrical bending	1411-1478	m-s
CO <sub>2</sub> symmetrical stretching	1392-1434	m-s
CH <sub>3</sub> symmetrical bending	1324-1373	w-m
CH <sub>3</sub> rocking	1008-1038, 1041-1060	w-m
C-C stretching	909 - 990	w-m
CO <sub>2</sub> symmetrical bending	631 - 701	m-s
CO <sub>2</sub> rocking	602-651, 346-568	w-s
Acetate Librational Modes	268-275, 276-286 287-303, 304-322	vw-w

temperature, it has been shown that the bands are resolved into discrete frequencies which are possibly due to hydrogen bonds of different lengths. The only acetate absorptions that did not intensify or sharpen at liquid nitrogen temperature were those in the  $250\text{--}350\text{ cm}^{-1}$  segment of the cesium bromide region. These absorptions actually appear to decrease in intensity and become more undefined at lowered temperature than at room temperature. This is one reason why they were tentatively assigned to a librational motion of the whole molecule within the crystal structure, because lowered temperature should have this effect on bands of such an assignment.

#### D. Isotopic Exchange

Exchange of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  as the coordinated water in the hydrated acetates is extremely useful in determining coordinated water frequencies. The  $\text{D}_2\text{O}$  absorption bands show similar form to the  $\text{H}_2\text{O}$  bands but are displaced by approximately a mass effect of  $1/\sqrt{2}$ . Generally the  $\text{D}_2\text{O}$  stretching region of the deuterated hydrates showed better splittings at liquid nitrogen temperature than did the normal hydrates in the  $\text{H}_2\text{O}$  stretching region. This may be due to the fact that since water vapor, which is present in the atmosphere, absorbs both sample and reference beams, therefore pen response and hence proper resolution is lessened in this region. There is no atmospheric

absorption in the  $D_2O$  stretching region, except for the  $2350\text{ cm.}^{-1}$   $CO_2$  absorption, and hence resolution is probably much better in this region, thus accounting for the better splittings found experimentally in the  $D_2O$  stretching region of the deuterated hydrates. Very little has been published in the literature concerning the exchange of  $D_2O$  for  $H_2O$  as the coordination water in complex metallic hydrates, and this technique should be extremely useful in future infrared investigations of the water of hydration in complex metallic hydrates.

#### E. Bonding and Structure of the Hydrated Acetates

##### 1. Tetrahydrate Acetates.

##### a. Nickel, cobalt and magnesium acetates $.4H_2O$ .

From the infrared analysis it can be concluded that nickel, cobalt, and magnesium tetrahydrate acetates have basically the same structure and this substantiates the X-ray data. Free water protons are present in the structures of these three hydrates, while the remainder of the water molecule protons that are present are important in the formation of intra- and inter- molecular hydrogen bonds. The splitting of the broad  $H_2O$  stretching absorption at liquid nitrogen temperature indicates that hydrogen bonds of different lengths are present in the structures of nickel, cobalt, and magnesium tetrahydrate acetates. Two of the coordinated water absorptions in the  $700-900\text{ cm.}^{-1}$  region at  $724-745\text{ cm.}^{-1}$  and  $803-813\text{ cm.}^{-1}$  appear to

be associated with the water molecules containing the free water protons. This fact is evidenced by the spectrum of nickel acetate  $\cdot 2\text{DOH} \cdot 2\text{H}_2\text{O}$ , where only the free water protons have been changed to deuterium atoms while the hydrogen bonded water protons remain as ordinary water. This is also evidenced by the  $\text{D}_2\text{O}$  solution spectra of nickel, cobalt, and magnesium acetates  $\cdot 4\text{H}_2\text{O}$ , which in solution do not contain free water protons, and show the disappearance of the same two absorptions. The infrared analysis indicates that the metal-water bonds possess covalent character in nickel, cobalt, and magnesium tetrahydrate acetates.

b. Manganese acetate  $\cdot 4\text{H}_2\text{O}$ . The infrared analysis indicates that manganese acetate  $\cdot 4\text{H}_2\text{O}$  has a structure similar to cobalt, nickel, and magnesium tetrahydrate acetates, except that there are no free water protons present. Thus all the water molecules are involved in the formation of intra- and intermolecular hydrogen bonds. Manganese acetate  $\cdot 4\text{H}_2\text{O}$  gives further evidence that two of the three coordinated water absorptions in the  $700\text{-}900\text{ cm}^{-1}$  region are associated with water molecules containing the free water protons because this hydrate, which does not contain free water protons, shows essentially only one water absorption in the  $700\text{-}900\text{ cm}^{-1}$  region. The low temperature splitting of the broad  $\text{H}_2\text{O}$  stretching absorption distinguishes different types of hydrogen bonded water protons in the structure

of manganese acetate  $.4\text{H}_2\text{O}$ . Covalent character is indicated for the metal-water bonds in this tetrahydrate acetate.

## 2. Trihydrate Acetates.

a. Lead acetate  $.3\text{H}_2\text{O}$ . The infrared spectra of lead acetate  $.3\text{H}_2\text{O}$  and the deuterated analog show only water bending and stretching absorptions and give no evidence of a splitting of the hydrogen bonded water stretching absorption at liquid nitrogen temperature. All coordinated water molecule protons in this trihydrate are involved in the formation of hydrogen bonds, and no evidence is given for a difference in the hydrogen bond lengths. There is no infrared evidence for covalent character of the ligand-metal bonds in lead acetate  $.3\text{H}_2\text{O}$ .

b. Sodium acetate  $.3\text{H}_2\text{O}$ . The infrared analysis of sodium acetate  $.3\text{H}_2\text{O}$  and sodium acetate  $.3\text{D}_2\text{O}$  indicates that there are no free water protons present, and that all of the water molecule protons are involved in the formation of hydrogen bonds. The spectrum of sodium acetate  $.3\text{H}_2\text{O}$  differs considerably from that of lead acetate  $.3\text{H}_2\text{O}$ . The infrared spectra of sodium acetate trihydrate and the deuterated analog shows a considerable splitting of the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching absorptions at low temperature, indicating that different types of hydrogen bonded water protons are present in the structure. Infrared



analysis does indicate the possibility of both intra- and inter-molecular hydrogen bonding being of importance in the structure of the hydrate. Sodium acetate  $\cdot 3\text{H}_2\text{O}$  shows a coordinated water absorption in the  $700\text{--}900\text{ cm}^{-1}$  region and also librational water absorptions in the cesium bromide region. The analysis indicates that covalent character is attached to the metal-water bonds in the structure of sodium acetate  $\cdot 3\text{H}_2\text{O}$ .

### 3. Dihydrate Acetates.

a. Cadmium acetate  $\cdot 2\text{H}_2\text{O}$ . There are no free water protons present in the structure of cadmium acetate  $\cdot 2\text{H}_2\text{O}$ . All water protons are involved in hydrogen bonding. There is no great difference between the hydrogen bonded water protons because no splitting of the broad  $\text{H}_2\text{O}$  stretching absorption occurs at liquid nitrogen temperature. No coordinated water absorptions are present in either the  $700\text{--}900\text{ cm}^{-1}$  region or in the far infrared region, and there is no evidence of covalent character of the metal-water bonds in cadmium acetate  $\cdot 2\text{H}_2\text{O}$ .

b. Lithium acetate  $\cdot 2\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  stretching region of the dihydrate and the  $\text{D}_2\text{O}$  stretching region of the deuterated hydrate show well defined splittings at liquid nitrogen temperature indicating that the hydrogen bonded water protons are involved in hydrogen bonds of different lengths. No

free water protons are present. Since coordinated water absorptions are present in the  $700\text{--}900\text{ cm}^{-1}$  region and in the far infrared region, this would indicate a covalent nature of the metal-water bonds in lithium acetate  $\cdot 2\text{H}_2\text{O}$ .

c. Zinc acetate  $\cdot 2\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching regions of the dihydrate and the deuterated hydrate, respectively, show definite splittings at liquid nitrogen temperature, indicating different hydrogen bond lengths for the water protons. No free water protons are present. Coordinated water absorptions are present in both the  $700\text{--}900\text{ cm}^{-1}$  and cesium bromide regions indicating some degree of covalent character of the metal-water bonds. X-ray data indicate a two-dimensional sheet structure for both lithium and zinc dihydrate acetates. The infrared analysis also indicates a similar structure for these hydrates.

#### 4. Monohydrate Acetates.

a. Calcium acetate  $\cdot \text{H}_2\text{O}$ . All water protons in this hydrate are important in hydrogen bonding. From the low temperature splitting of the  $\text{H}_2\text{O}$  stretching absorption into two peaks, and the  $\text{D}_2\text{O}$  stretching absorption into four peaks, hydrogen bonds of different lengths are probably present in the structure. Since no coordinated water absorptions appear in the  $700\text{--}900\text{ cm}^{-1}$  region, there is no evidence for covalent

character of the metal-water bonds from the infrared analysis.

b. Chromic acetate  $\cdot\text{H}_2\text{O}$ . There are no free water protons present in the structure of chromic acetate  $\cdot\text{H}_2\text{O}$ , and all of the water protons are important in the formation of hydrogen bonds. The broad  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching absorptions of the hydrate and the deuterated hydrate, respectively, show no splitting at low temperature and indicate that there is no major difference of the hydrogen bonded water protons. There are no coordinated water absorptions in the  $700\text{-}900\text{ cm}^{-1}$  region and there is no evidence for covalent character of the metal-water bonds in the structure of chromic acetate  $\cdot\text{H}_2\text{O}$ .

c. Cupric acetate  $\cdot\text{H}_2\text{O}$ . The infrared analysis substantiates the X-ray data which indicates different hydrogen bond lengths for the water protons. The broad  $\text{H}_2\text{O}$  stretching absorption shows a definite splitting at liquid nitrogen temperature. All water protons are involved in the formation of hydrogen bonds and there are no free water protons present in the structure of cupric acetate  $\cdot\text{H}_2\text{O}$ . No coordinated water absorptions are present in the  $700\text{-}900\text{ cm}^{-1}$  region and there is no infrared evidence for covalent character of the metal-water bonds of cupric acetate monohydrate.

5. Strontium Acetate  $\cdot\frac{1}{2}\text{H}_2\text{O}$ . No free water protons are present in the structure and all water molecule protons

are important in hydrogen bonding. The  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  stretching regions of the hydrate and the deuterated hydrate show definite splittings at both room temperature and at liquid nitrogen temperature. Thus hydrogen bonds of different strengths are probably present in the structure. Since a coordinated water absorption appears which is assigned to a wagging, twisting, or rocking mode, there is probably some covalent character attached to the metal-water bonds of strontium acetate  $\cdot \frac{1}{2}\text{H}_2\text{O}$ .

#### 6. Basic Hydrated Acetates.

##### a. Basic aluminum and basic thorium acetates $\cdot \text{H}_2\text{O}$ .

These hydrates contain OH groups bound directly to the metal and also coordinated water molecules. A high frequency, sharp absorption appears in the spectra of both basic acetates which is indicative of the free stretching of OH groups bound to the metal. This absorption occurs at a higher frequency and is sharper than the free water proton absorption that was found in some of the tetrahydrate acetates. The hydrogen bonded water stretching absorption in basic aluminum and basic thorium acetates  $\cdot \text{H}_2\text{O}$  shows no structure at liquid nitrogen temperature and indicates that all of the coordinated water protons are involved in hydrogen bonding. There are no coordinated water absorptions in the  $700\text{--}900\text{ cm}^{-1}$  region in either basic hydrate and no evidence is present that would substantiate covalent character of the metal-water bonds. The strong absorption at

978  $\text{cm}^{-1}$  in basic aluminum acetate overlaps the C-C stretch, and is probably due to the Al-O-Al linkage.

#### F. Proton Nuclear Magnetic Resonance.

Integrated proton nuclear magnetic resonance spectra of the hydrated acetates have given the number of coordinated water molecules per molecule of acetate. This information is useful since it shows that there is no randomly absorbed water present in the crystal lattice of the hydrates, and that the water molecules present occupy definite coordination positions. Proton nuclear magnetic resonance has also been used to determine the per cent purity of the deuterated hydrates. Proton NMR spectra of the anhydrous and dehydrated acetate complexes showed that no water was present in the lattice, thus insuring the fact that the anhydrous acetates were indeed anhydrous and that the dehydrated compounds had in fact been completely dehydrated.

#### G. Suggestions for Further Work.

Without previous knowledge, it would be thought that the exchange of  $\text{D}_2\text{O}$  for  $\text{H}_2\text{O}$  as the coordination water in the metallic acetate hydrates should be a rapid and simple procedure. It was found, however, that the reaction proceeded very slowly at room temperature and difficulty was encountered in obtaining a high purity of the deuterated hydrate. It should be very interesting to study the kinetics of this exchange reaction.

Many absorptions were found, especially in the tetrahydrate acetates, in the far infrared region which have been assigned to the librational modes of the coordinated water. The absorptions generally showed splitting and an appreciable shift upon observation at liquid nitrogen temperature. It would be interesting to precisely depict the exact nature, specific assignments, and the exact motion of the water molecules which give rise to these librational modes.

X-ray diffraction data was not available for the majority of the hydrated acetate complexes studied. It would be interesting to determine X-ray structures for these complexes to see if they tend to substantiate the type of bonding indicated by the infrared analysis.

## PART V

## LITERATURE CITED

1. Addison, C. C. and Gatehouse, B. M., J. Chem. Soc., 613 (1960).
2. Amirthalingam, V. and Padmanabhan, V. M., Acta Cryst., 11, 896 (1958).
3. Barraclough, C. G., Lewis, J., and Nyholm, R. S., J. Chem. Soc., 3552 (1959).
4. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules", 2nd ed., John Wiley & Sons, New York (1958).
5. Bernal, J. D. and Fowler, R. H., J.Chem.Phys. 1, 515 (1933).
6. Bok, L. D. C. and Geib, K. H., Naturwissenschaften, 26, 122 (1938).
7. Bragg, W.H. and Morgan, G.T., Proc. Roy. Soc. (London), A104, 437 (1923).
8. Cartwright, C.H., Phys. Rev., 49, 470 (1936).
9. Childers, E. and Struthers, G.W., Anal.Chem., 27, 737 (1955).
10. Crawford, B.L., Jr. and Wilson, E.B., Jr., J. Chem. Phys., 9, 323 (1941).
11. Dieke and Duncan, "Spectroscopic Properties of Uranium Compounds", McGraw-Hill Book Co., New York, (1949).
12. Duval, C., Lecomte, J. and Douville, F., Ann.Phys., 17, 5 (1942).
13. Ferraro, J.R., Inorg. Nucl. Chem., 10, 319 (1959).
14. Ferraro, J.R., J. Mol. Spec., 4, 99 (1960).
15. Ferraro, J.R., J. Chem. Ed., 38, 201 (1961).
16. Figgis, B.N. and Martin, R.L., J.Chem.Soc., 3837 (1956).
17. Fujita, J., Nakamoto, K. and Kobayashi, M., J. Am. Chem. Soc., 78, 3295 (1956).

18. Fujita, J., Nakamoto, K. and Kobayashi, M., ibid., 78, 3963 (1956).
19. Fujita, J. Nakamoto, K. and Kobayashi, M., J. Phys. Chem., 61, 1014 (1957).
20. Gamo, I., Bull. Chem.Soc. Japan, 34, 760 (1961).
21. Gamo, I., ibid., 34, 764 (1961).
22. Gamo, I., ibid., 34, 1430 (1961).
23. Gamo, I., ibid., 34, 1433 (1961).
24. Gatehouse, B. M., Livingstone, S. E. and Nyholm, R. S., J. Chem. Soc., 4222 (1957).
25. Gatehouse, B. M., Livingstone, S. E., and Nyholm, R. S., ibid., 3137 (1958).
26. Gatehouse, B. M. and Comyns, A. E., J. Chem. Soc., 3965 (1958).
27. Giguère, P.A. and Harvey, K.B., Can.J.Chem., 34, 798 (1956).
28. Griffith, W.P., Lewis, J., and Wilkinson, G., J. Inorg. Nucl. Chem., 7, 38 (1958).
29. Halford, J.O. and Anderson, L.C., J.Am.Chem.Soc., 58, 736 (1936)
30. Hass, M. and Sutherland, G.B.B.M., F.R.S., Proc.Roy.Soc., (London), A236, 427 (1956).
31. Herzberg, G., "Molecular Spectra and Molecular Structure", Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules", 1st ed., D. van Nostrand Co., Inc., New York (1945).
32. Holtzclaw, H.F., Jr. and Collman, J.P., J. Am. Chem. Soc., 79, 3318 (1957).



33. Hunt, J.M. and Turner, D.S., Anal.Chem., 25, 1169 (1953).
34. Hunt, J.M., Wisherd, M.P. and Bonham, L.D., Anal. Chem., 22, 1478 (1950).
35. Ito, K. and Bernstein, H.J., Can.J.Chem., 34, 170 (1956).
36. Jones, L.H., J. Chem. Phys., 22, 217 (1954).
37. Jones, L.H. and McLaren, E., ibid., 22, 1796 (1954).
38. Jones, L. H., ibid., 23, 2105 (1955).
39. Jones, R.N., Natl.Res. Council Bull. No. 6, Ottawa (1959).
40. Jones, R.N., Humphries, P., Herling, F., and Dobriner, K., J. Am. Chem. Soc., 73, 3215 (1951).
41. Jørgensen, C. K., "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, London, (1962).
42. King, W.T., and Crawford, B., Jr., J.Mol.Spectroscopy, 5, 421 (1960).
43. Koyama, H. and Saito, Y., Bull.Chem.Soc.Japan, 127, 113 (1954).
44. Lawson, K.E., "Infrared Absorption of Inorganic Substances", Reinhold Publishing Corp., New York, (1961).
45. Lecomte, J., Cahiers Phys., 17, 1 (1943).
46. Lecomte, J., Anal.Chim.Acta., 2, 727 (1948).
47. Lecomte, J., Disc. Faraday Soc., 9, 125 (1950).
48. Levy, L. Walter- and Soleilhavoup, I., Comp.Rend., 238, 1421. (1954).
49. Levy, L. Walter-, Soleilhavoup, I., and de Wolff, P. M., ibid., 249, 1234 (1959).

50. Lewis, J., Irving, R.J., and Wilkinson, G., J. Inorg. Nucl. Chem., 7, 32 (1958).
51. Lucchesi, P.J. and Glasson, W.A., J. Am. Chem. Soc., 78, 1347 (1956).
52. Lyon, W. and Kinsey, E.L., Phys.Rev., 61, 482 (1942).
53. Matsumura, O., Mem.Fac.Sci., Kyusyu Univ., Ser.B, 1, 1 (1951).
54. McGrath, J.W. and Silvidi, A.A., J.Chem.Phys., 34, 322 (1961).
55. Miklukhin, G.P., Doklady Akad. Nauk. S.S.S.R., 70, 437 (1950).
56. Miklukhin, G.P., Zhur. Fiz. Khim., 25, 688 (1951).
57. Miklukhin, G.P. and Rekasheva, A.F., Doklady Akad. Nauk. S.S.S.R., 101, 881 (1955).
58. Miller, F.A. and Wilkins, C.H., Anal.Chem., 24, 1253 (1952).
59. Miller, F.A., Carlson, G.L., Bentley, F.F., and Jones, W.H., Spectrochim. Acta, 16, 135 (1960).
60. Nakamoto, K., Margoshes, M., and Rundle, R.E., J. Am. Chem. Soc., 77, 6480 (1955).
61. Nakamoto, K., Fujita, J., Tanaka, S., and Kobayashi, M., J. Am. Chem. Soc., 79, 4904 (1957).
62. Nakamoto, K., Morimoto, Y., and Martell, A.E., J. Am. Chem. Soc., 83, 4528 (1961).
63. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, New York, (1963), p. 198.
64. Ockman, N., Diss. Abstr., 18, 1466 (1958).
65. Ockman, N., Adv. in Phys., 7, 199 (1958).
66. Orgel, L.E., "An Introduction to Transition - Metal Chemistry: Ligand Field Theory", John Wiley & Sons, New York, (1960).

67. Padmanabhan, V.M., Current Sci. (India), 21, 97 (1952).
68. Penland, R.B., Mizushima, S., Curran, C., and Quagliano, J.V., J. Am. Chem. Soc., 79, 1575 (1957).
69. Pimentel, G.C. and McClellan, A.L., "The Hydrogen Bond", W. H. Freeman & Co., San Francisco, (1960).
70. Pople, J.A., Schneider, W.G., and Bernstein, H.V., "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, Inc., New York, (1959).
71. Sartori, G., Furlani, C., and Damiani, A., J. Inorg. Nucl. Chem., 8, 119 (1958).
72. Sen, D.N., Mizushima, S., Curran, C., and Quagliano, J.V., J. Am. Chem. Soc., 77, 211 (1955).
73. Shimizu, H. and Weller, S., J. Am. Chem. Soc., 74, 4469 (1952).
74. Svatos, G.F., Curran, C., and Quagliano, J.V., J. Am. Chem. Soc., 77, 6159 (1955).
75. Ueno, K. and Martell, A.E., J. Phys. Chem., 59, 998 (1955).
76. van Niekerk, J.N., and Schoening, F.R.L., and (in part) de Wet, J.F., Acta Cryst., 6, 501 (1953).
77. van Niekerk, J.N. and Schoening, F.R.L., ibid., 6, 227 (1953).
78. van Niekerk, J.N. and Schoening, F.R.L., ibid., 6, 609 (1953).
79. van Niekerk, J.N., Schoening, F.R.L., and Talbot, J.H., ibid., 6, 720 (1953).
80. van Niekerk, J.N. and Schoening, F.R.L., Nature, 171, 36 (1953).
81. van der Elsen, J. and Robinson, D.W., Spectrochim. Acta, 17, 1249 (1961).
82. Vedder, W. and Hornig, D.F., Adv. in Spectroscopy, Vol. II, Interscience Publishers, Inc., New York, 189 (1961).
83. Vedder, W. and Hornig, D.F., J. Chem. Phys., 35, 1560 (1961).

84. Wells, A.J. and Wilson, E.B., Jr., J. Chem. Phys., 9, 314 (1941).
85. Wiberley, S.E., Ulrich, R.E., and Casali, L., Unpublished Work.
86. Wilmshurst, K.J., J. Chem. Phys., 23, 2463 (1955).
87. Wilson, E.B., Jr., Decius, J.C., and Cross, P.C., "Molecular Vibrations", McGraw-Hill Book Co., Inc., New York, (1955).
88. Wilson, T.P., J. Chem. Phys., 11, 361 (1943).
89. Wyckoff, R.W.G., "Crystal Structures", Interscience Publishers, Inc., New York, Vol. I (1948); Vol. II (1951); Vol. III (1953).
90. Yamaguchi, A., Penland, R.B., Mizushima, S., Lane, T.J., Curran, C., and Quagliano, J.V., J. Am. Chem. Soc., 80, 527 (1958).
91. Zachariasen, W.H. and Pettinger, H.A., Acta Cryst., 12, 526 (1959).

## ADDENDUM

Two recent studies which are pertinent to this work were evidenced after the final preparation of the Thesis and are thus missing from Part V, but are included here for reference:

1), G. E. Walrafen (J. Chem. Phys. in press) has studied the infrared and Raman frequencies of water and heavy water, and the intermolecular vibrations of water have been related to a five-molecule hydrogen bonded  $C_{2v}$  model which is consistent with the X-ray data. The librational frequencies of water at 450 and approximately  $780\text{ cm}^{-1}$  shift to lower frequencies by the approximate ratio of  $\sqrt{2}$  or less in heavy water, and the O-H....O bending and stretching vibrations at 60 and  $175\text{ cm}^{-1}$  were found to exhibit nearly identical frequencies in water and heavy water. Satisfactory agreements were found between the observed polarizations and the polarizations predicted for  $C_{2v}$  symmetry. Detailed librational assignments depend upon the expectation that the highest librational frequency is related to the lowest of the three moments of inertia of  $H_2O$  and upon the fact that the  $A_2$  mode which is infrared forbidden, corresponds to the Raman band at  $450\text{ cm}^{-1}$ . The remaining librational frequency falls within the range of the other two.

2). Shevchenko has studied the infrared absorption spectra of some metallic acetates (Ukrain. Khim. Zhur., 29, 1247-1250 (1963)), but at this time a copy of the paper was not available.